

AD-752 594

PLASTIC MATERIALS FOR EYE PROTECTION
FROM LASERS

Allan E. Sherr, et al

American Cyanamid Company

Prepared for:

School of Aerospace Medicine

October 1972

DISTRIBUTED BY:

NTIS

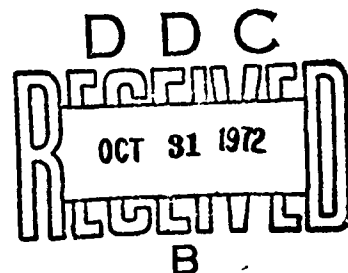
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

AD752594

PLASTIC MATERIALS FOR EYE PROTECTION FROM LASERS

ALLAN E. SHERR, Ph.D.
WILLIAM F. CORDES, III, Ph.D.
and
ROBERT J. TUCKER, B.S.
AMERICAN CYANAMID COMPANY

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151



Prepared For: USAF School of Aerospace Medicine
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas

Approved for public release; distribution unlimited

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

| | | | |
|--|--|---|------------------------------|
| 1. ORIGINATING ACTIVITY (Corporate author) American Cyanamid Company Organic Chemicals Division Bound Brook, New Jersey 08805 | | 2a. REPORT SECURITY CLASSIFICATION Unclassified | |
| | | 2b. GROUP N/A | |
| 3. REPORT TITLE Plastic Materials for Eye Protection from Lasers | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) 3 May 1971 - 15 July 1972 | | | |
| 5. AU THOR(S) (First name, middle initial, last name) Allan E. Sherr, William F. Cordes, III and Robert J. Tucker | | | |
| 6. REPORT DATE October 1972 | | 7a. TOTAL NO. OF PAGES 98 | 7b. NO. OF REFS 27 |
| 8a. CONTRACT OR GRANT NO. F41609-71-C-0019 | | 8b. ORIGINATOR'S REPORT NUMBER(S) | |
| 9. PROJECT NO. 7784 | | | |
| 10. Task No. 778402 | | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | |
| 11. Work Unit Number 778402014 | | | |
| 12. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited | | | |
| 11. SUPPLEMENTARY NOTES | | 12. SPONSORING MILITARY ACTIVITY USAF School of Aerospace Medicine Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235 | |
| 13. ABSTRACT <p>Plastic goggles were produced which offer protection against several lasers. The goggles had a minimum optical density of 3 at 300-400, 840, 1,060, 780-1,760 and 2,755 to 14,000 nm. Cast plastic sheet was prepared which had similar protective capabilities.</p> <p>Over 300 organic compounds were evaluated and/or synthesized as possible near infrared absorbing compounds. Several of these structural systems offer promise for laser protection.</p> <p>The compounds were evaluated in a variety of plastics including cellulose propionate, polymethyl methacrylate, polycarbonate, polyethylene terephthalate, and polyvinyl chloride. The propionate and methacrylate were the polymers of choice for most of the work.</p> <p>Cadmium stannate was investigated as an absorber and was shown to have some interesting spectral properties.</p> <p>A discussion is presented on the correlation between structure and spectral properties of several of the compounds studied.</p> | | | |

Ia

DD FORM 1473

Unclassified

Security Classification

PLASTIC MATERIALS FOR EYE PROTECTION FROM LASERS

ALLAN E. SHERR, Ph.D.
WILLIAM F. CORDES, III, Ph.D.
and
ROBERT J. TUCKER, B.S.

IC

FOREWORD

This report was prepared by personnel of American Cyanamid Company, Organic Chemicals Division, Bound Brook, N. J. The Contract Monitor was Captain Donald R. Marston of the Ocular-Thermal Branch, Radiobiology Division.

The research was performed under Project Number 7784. It was funded by the USAF School of Aerospace Medicine under Contract No F41609-71-C-0019. The work was accomplished between 3 May 1971 and 15 July 1972. This report was submitted for publication on October 2, 1972.

The principal investigator was Allan E. Sherr. The major work on producing the goggles and cast sheet as well as the evaluations in plastic was done by Robert J. Tucker. The major synthetic effort on this contract was done by Mrs. N. A. Weston, Miss R. A. Greenwood, Dr. P. J. Belling and Dr. W. F. Cordes, III. Miss Greenwood assisted in plastic evaluation and spectral searches for near infrared absorbing species. The Cd_2SnO_4 work was done by Dr. A. J. Nozik of our Stamford, Connecticut Research Laboratories.

The principal investigator expresses his gratitude for the excellent cooperation and assistance of these individuals, as well as that of the staff at the USAF School of Aerospace Medicine.

ABSTRACT

Plastic goggles were produced which offer protection against several lasers. The goggles have a minimum optical density of at least 3 at 0.3-0.4, 0.84, 0.78-1.76 and 2.755 to 14.0 μm and at least 4 at 1.06 μm . Cast plastic sheet was prepared which had similar protective capabilities.

Over 300 organic compounds were evaluated and/or synthesized as possible near infrared absorbing compounds. Several of these structural systems offer promise for laser protection.

The compounds were evaluated in a variety of plastics including cellulose propionate, polymethyl methacrylate, polycarbonate, polyethylene terephthalate, and polyvinyl chloride. The propionate and methacrylate were the polymers of choice for most of the work.

Cadmium stannate was investigated as an absorber and was shown to have some interesting spectral properties.

A discussion is presented on the correlation between structure and spectral properties of several of the compounds studied.

TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| I. Introduction | |
| Purpose of Study | 1 |
| Background | 1 |
| II. Results | |
| A. Absorbers | 7 |
| 1. Type I Compounds | 12 |
| 2. Type II Compounds | 13 |
| 3. Type III Compounds | 22 |
| 4. Type IV Compounds | 26 |
| 5. Type V Compounds | 26 |
| 6. Type VI Compounds | 28 |
| 7. Type VII Compounds | 29 |
| 8. Miscellaneous Compounds | 29 |
| B. Evaluations With Plastics | 41 |
| 1. Cellulose Propionate | 45 |
| 2. Polycarbonate | 52 |
| 3. Polymethyl Methacrylate | 55 |
| 4. Cadmium Stannate | 58 |
| 5. Miscellaneous Polymers | 65 |
| 6. Physical System of Attenuating from 1.9-2.3 μ m | 65 |
| C. Deliverable Items | 66 |

TABLE OF CONTENTS - Continued

| | <u>Page</u> |
|--|-------------|
| III. Conclusions | |
| A. Spectral Correlations of Some Near-Infrared Absorbers | 69 |
| 1. Substituent Effects | 69 |
| 2. Effect of Different Metal Atoms | 72 |
| 3. Effect of Additional Fused Aromatic Rings | 75 |
| 4. Effect of N, S, O Coordination | 76 |
| B. Recommendations | 81 |
| References | 87 |

FIGURES AND ILLUSTRATIONS

| <u>Table No</u> | | <u>Page</u> |
|-----------------|--|-------------|
| I | Laser Protective Spectacles | 3 |
| II | Laser Protective Visor, Filter Type A | 3 |
| III | Laser Protective Visor, Filter Type B | 4 |
| IV | Type A Compounds | 14 |
| V | Type B Compounds | 15 |
| VI | Type D Compounds | 18 |
| VII | Type E Structures | 19 |
| VIII | Type F Compounds | 21 |
| IX | Type III Compounds | 23 |
| X | Squaric Acid Type Compounds | 27 |
| XI | Miscellaneous Compounds | 30 |
| XII | Spectral Data for Several Plastics | 42 |
| XIII | Absorption of Plastics at CO ₂ Wavelength | 45 |
| XIV | Formulations in Cellulose Propionate | 50 |
| XV | Comparison of Propionates | 51 |
| XVI | PMMA Casting Mixes | 57 |
| XVII | Surface Pretreatment of Acrylite | 61 |
| XVIII | Effect of Power and Pressure on Surface Temperature | 62 |
| XIX | Film Formation on Various Substrates | 63 |
| XX | Compounds and NIR Spectra | 74 |
| XXI | Change of Coordinating Group V or VI Atoms | 77 |
| XXII | Change from Dithiol Coordination to Diamine | 79 |

Figure No

Page

| | | |
|---|--|----|
| 1 | LASER-GARD® Lens Neodymium-Gallium Arsenide | 5 |
| 2 | GLENGARD® IREx® Lens, 2" x 4-1/4", Shade 5 | 6 |
| 3 | Visibly Opaque Filter R7511-9 | 44 |
| 4 | Near IR Transmission Spectra of Cd_2SnO_4 Thin Films | 59 |

LIST OF ABBREVIATIONS

| <u>Abbreviation</u> | <u>Meaning</u> |
|---------------------|---|
| α | activity (l/g-cm) |
| AIBN | azobisisobutyronitrile |
| CP | cellulose propionate |
| CTE | coefficient of thermal expansion |
| DMF | dimethyl formamide |
| DMSO | dimethyl sulfoxide |
| ϵ | molar absorptivity |
| FOM | Carbon Arc Fade-Ometer, temperature $100 \pm 5^\circ\text{F}$ |
| Lit. | literature |
| MMA | methyl methacrylate |
| mg | milligrams |
| NIR | near-infrared absorber |
| nm | nanometers |
| O.D. | optical density |
| PC | phthalocyanine |
| PMMA | polymethyl methacrylate |
| PVC | polyvinyl chloride |
| sh | shoulder |
| Tg | glass transition temperature |
| THF | tetrahydrofuran |
| μm | micrometers |
| UV | ultraviolet |
| λ | wavelength in nanometers |
| Y | luminous transmittance |

PLASTIC MATERIALS FOR EYE PROTECTION FROM LASERS

I. INTRODUCTION

Purpose of the Study

This program was undertaken to develop an ophthalmically acceptable personnel filter that could be used as spectacle-goggles or as flight-helmet visors. The filter was to provide protection at wavelengths of interest for Q-switched, normal pulse and continuous wave lasers. The filter was to be a fixed absorbing filter composed of a plastic base material containing suitable absorbers for giving the desired protection.

Background

Additional ocular protection is required with the advent of operational laser systems. While an "omni protector" is a most desirable concept, it is not presently feasible at the current state of knowledge. American Cyanamid Company had previously developed plastic filter compositions which could provide protection against individual laser systems, or selected combinations of laser wavelengths (1-6), but had not been able to provide protection against a very wide variety of laser systems in one unit. In addition, American Cyanamid Company, and its subsidiary, Glendale Optical Company, had experience in providing plastics which absorbed infrared rays and nuclear flash radiation (7, 8).

It was agreed that the research emphasis for the filters would be put on the following:

1. Absorption (O.D.) of 3 or higher from 1-10 μm wavelength.
2. O.D. of 4 at the 0.694 μm and 1.06 μm wavelengths (the requirement for protection at 0.694 μm was later deleted).

3. Luminous transmittance of 65% or better, where luminous transmittance is defined as the transmission of electromagnetic radiation in the range between 380 and 780 nanometers weighted by the spectral sensitivity of the eye.
4. The filter material should be moldable or formable into various configurations such as visors for aircrew helmets, safety spectacle-goggles for ground personnel and sheeting for applicable enclosures.
5. All the filter requirements to be put into one filter material if possible.
6. Possible use of polycarbonate as a plastic base.

Priority was to be given to the items in the order listed.

It must be emphasized that laser testing of the filter materials developed was not part of this effort. These tests should be performed before any of the filters are utilized for personnel protection!

There were two major difficulties foreseen at the outset of this work. The first was attainment of 65% luminous transmittance while achieving an optical density (O.D.) of 4.0 or better at both 0.694 μm and 1.06 μm as well as optical density of 3 or better from 1.0 through 10 μm .

Table I summarizes the optical properties of laser protective spectacles prepared under Contract F41609-69-C-0055; Tables II and III show the optical properties of the two laser protective visors prepared under this previous Contract (6). This previous research indicated that a luminous transmittance of 65% would be difficult to obtain while simultaneously achieving optical densities of 4 at 0.694 μm and 1.06 μm . With the present state of our knowledge, we would expect to achieve a luminous transmittance of 25-30% maximum when the protective filter has an optical density of 4 or higher at both 0.694 and 1.06 μm .

Table I

Laser Protective Spectacles

| <u>Optical Density</u> | <u>Wavelength, μm</u> |
|------------------------|---|
| 4 | 1.06 |
| 3.7 | 0.840 |
| 4 | 0.6943 |
| 2.3 | 0.671 |
| 1.2 | 0.6328 |
| 4 | 0.530 |
| 5.5+ | 0.5145 |
| 5.5+ | 0.488 |
| 5.5+ | 0.300-0.400 |

Luminous Transmittance - 24-26%

Table II

Laser Protective Visor, Filter Type A

| <u>Optical Density</u> | <u>Wavelength, μm</u> |
|------------------------|---|
| 3.5-4.0 | 1.06 |
| 3.5-4.0 | 0.840 |
| 3.5-4.0 | 0.530 |
| 3.5-5.5+ | 0.5145 |
| 3.5-5.5+ | 0.488 |
| 3.5-5.5+ | 0.300-0.400 |

Color: Orange; Luminous Transmittance: 42-50%

Table III

Laser Protective Visor, Filter Type B

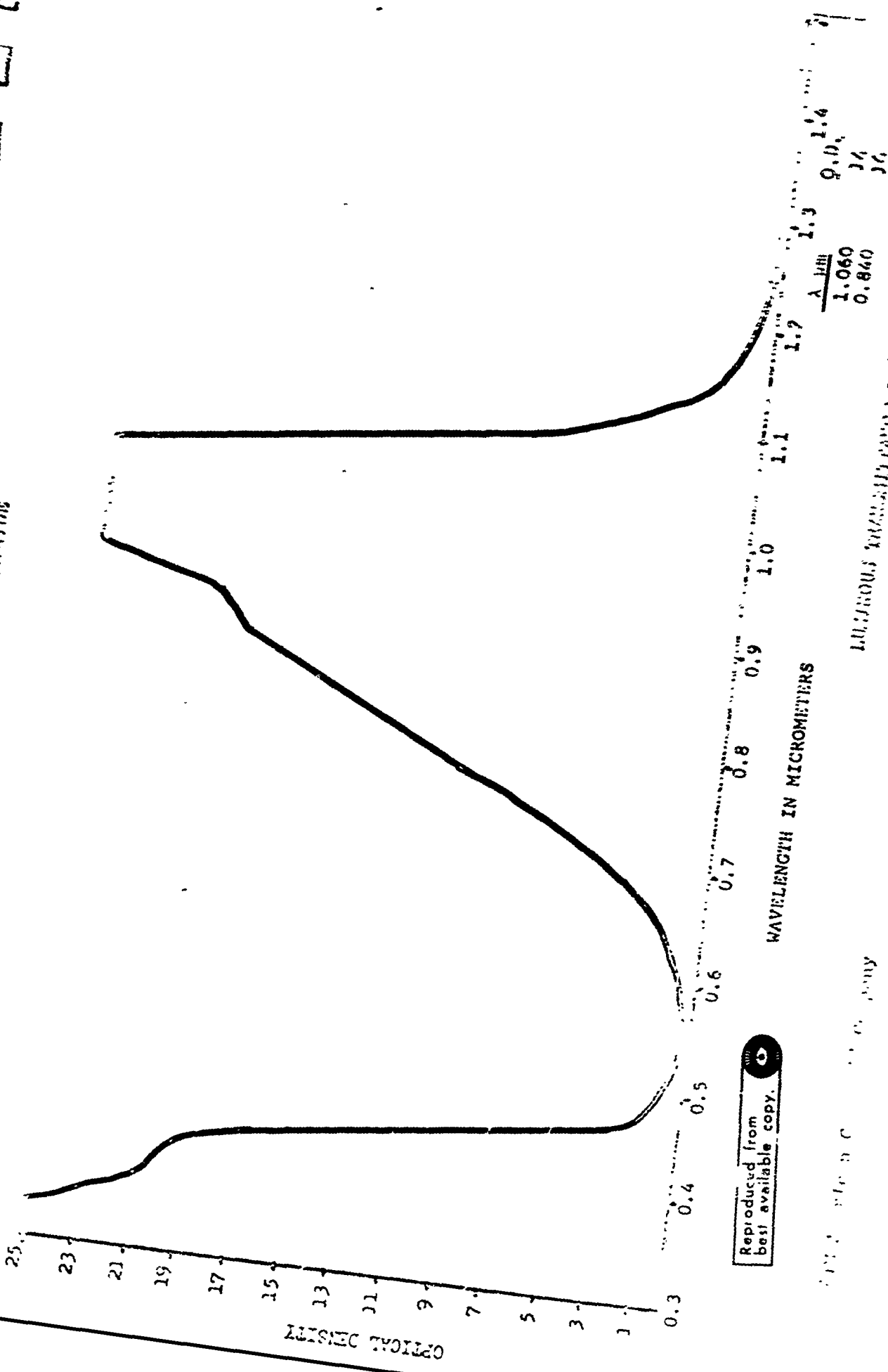
| <u>Optical Density</u> | <u>Wavelength, μm</u> |
|------------------------|---|
| 5.5 | 0.6943 |
| 3.3-3.5 | 0.671 |
| 1.7-1.9 | 0.633 |
| 3.5 | 0.200-0.400 |

Color: Blue; Luminous Transmittance: 50-53%

The second major difficulty would be to obtain an O.D. of 3.0 or better in the range 1.5 μm through 2.5 μm . Figure 1 indicates that a Neodymium-Gallium Arsenide filter does not offer protection beyond 1.1 μm . Figure 2 shows that the plastic IREX® welding filters do not have optical density of 3 or better from 1.85-2.5 μm even though they do offer protection from 1.0 μm through 2.5 μm in terms of welding arcs. From 2.5 μm to 6.0 μm our experience indicates that the plastic media itself will provide an optical density of 3 or better, this protection could even extend beyond 10.0 μm . Little is known about absorbers for the region 1.8-2.3 μm ; thus first research emphasis would be placed on evaluating candidate compounds to absorb in this spectral region.

Other problems anticipated were: the actual casting of plastic sheet to form visors; molding of the spectacles; compatibility problems; stability of the plastic systems to heat, light, weather, lasers, etc.

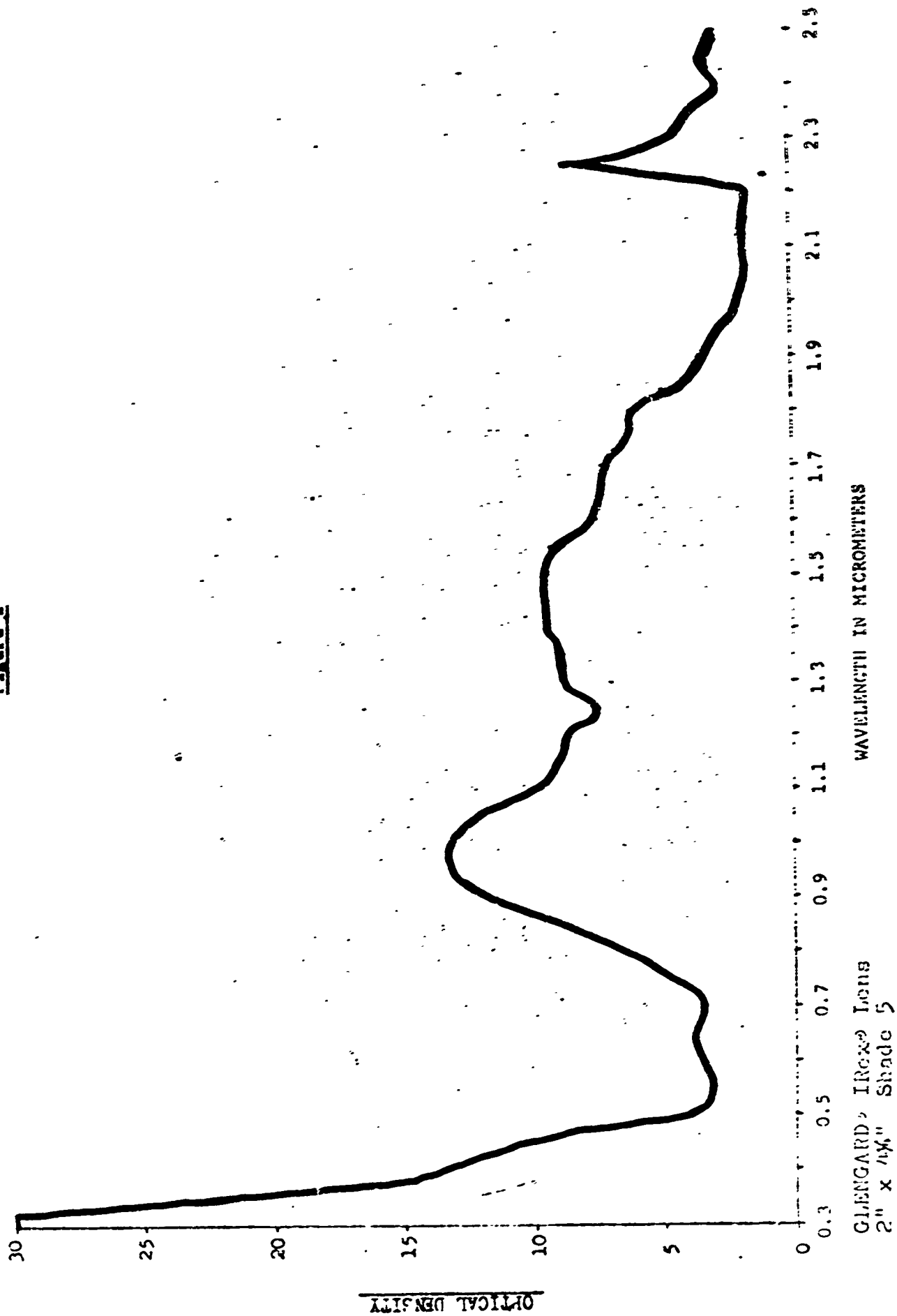
PLYMETHYL
 HYDROGEN
 GALACTIC ACETIC ACID



Reproduced from
 best available copy.

LUMINOUS TRANSMITTANCE 543

Figure 2

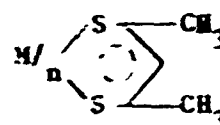
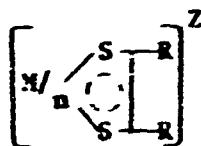
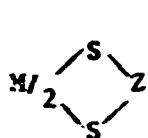


II. RESULTS

A. Absorbers

Materials absorbing in the 1.0-3.0 μ m region of the infrared spectrum with an appreciable extinction coefficient are generally those compounds which undergo optical intervalence transfer. Optical intervalence transfer can be defined as an optical transition involving a transfer of an electron from an essentially localized site to an adjacent one, where the donor and acceptor are metal ions possessing more than one accessible oxidation state. These transitions can occur between metal ions of the same element (homonuclear) or between metal ions of different elements (heteronuclear).

Some systems which undergo optical transitions in the region of interest are shown by structures I-VII.



Z equals C=NCS, C=C(CN)₂, R equals ϕ , CF₃, CN

C=S, RC, R₂NC, R₂P Z equals O, -1, -2

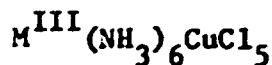
n equals 2, 3

M above can be any metal ion.

I

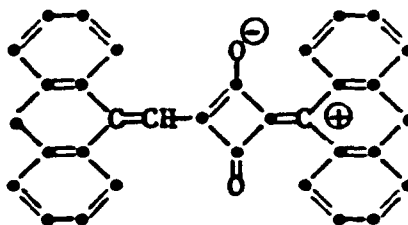
II

III

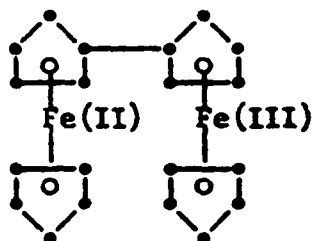


M = Co, Cr, Rh, Ru

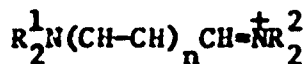
IV



V



VI



R is an alkyl or aryl group

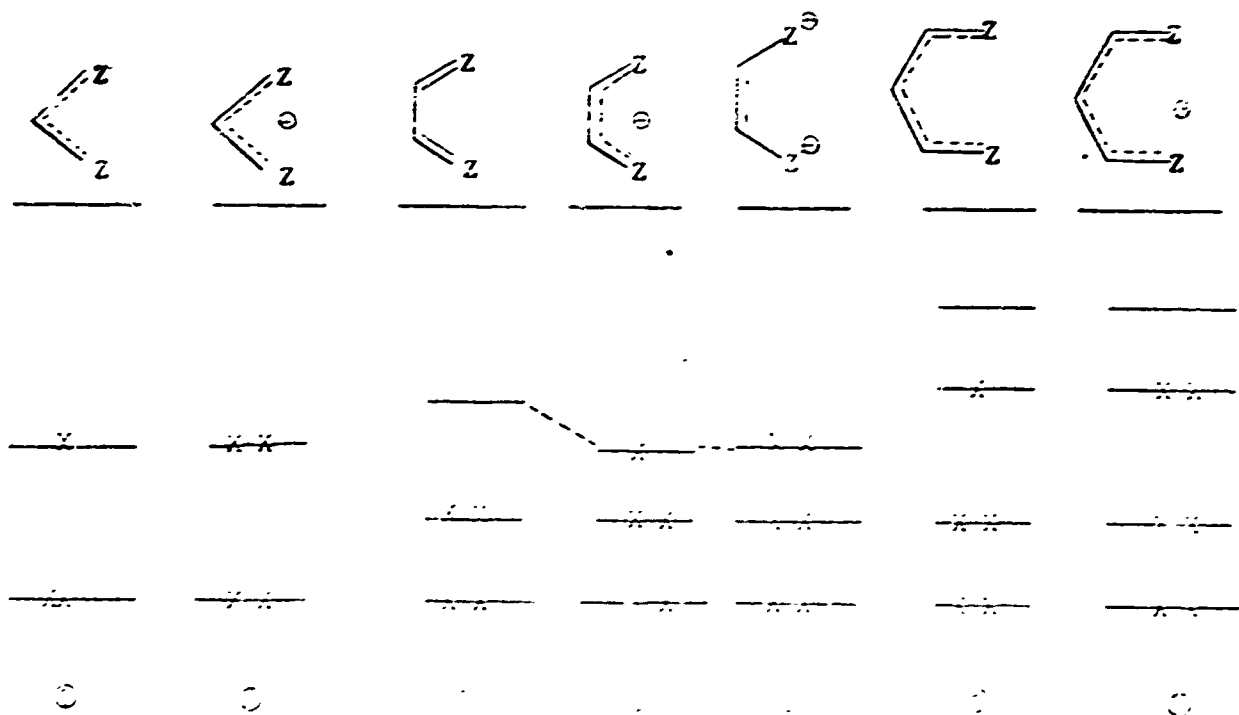
VII

Work with complexes of Type I has been done by Fackler (9). Models of this system are already familiar; namely, dithiocarbamates, xanthates, dithiophosphates, dithiophosphinates as nickel or zinc complexes.

Type II species have been prepared and studied by Holm (10), Gray (11) and Schrauzer (12). The flexibility of the Type II species is great. The species are capable of redox reactions, the ease of which is determined by R. Hence, desirable spectral properties might be enhanced or decreased by varying Z. One theory holds that electron density around the metal is relatively constant, while oxidation or reduction occurs by electron transfer in or out of low-lying ligand antibonding orbitals. M has been varied, i.e., Fe, Co, Ni, Pd, Pt, Re, W, Mo.

We extended the type II species further to include other hetero atoms such as oxygen or nitrogen. Using a simple topology argument, Schrauzer (13) suggested that those ligands containing an "even" number of vertical π orbitals should be preferred over those ligands containing an "odd" number of vertical π orbitals. This system of classification is based on the knowledge that an "odd" unsaturated ligand system will tend to exist as a monoanion due to the presence of a nonbonding singly occupied π molecular orbital according to its energy level diagram. Since there are no other low-lying π molecular orbitals present, the "odd" ligands do not accept additional electrons, and as a result, form metal complexes which do not show intense near-infrared absorption bands. It has been shown in the case of the four-atom "even" ligands, that the lowest unoccupied π molecular orbital is only weakly antibonding, if the two atoms at positions ① and ④ of the butadiene framework are sulfur.

A diagram depicting this concept is shown below.

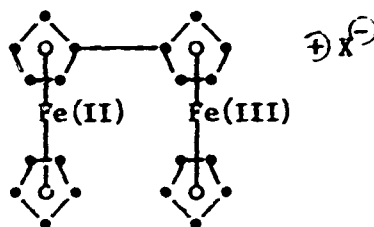


It should be pointed out that Z may equal oxygen, R-substituted nitrogen, sulfur, or combinations of these groups. This diagram indicates that the basic dithiodiketone structure (3) may also exist as the mono-anion (4) or the dianion (5).

Type III is more recent (14) but was appealing since the authors claim the sulfur chelates can be readily prepared by substitution of oxygen in acetylacetone by sulfur (H_2S). Because of the many possibilities existent with Types II and III, these were emphasized during the course of this investigation.

Compounds of Type IV were described by Allen and Hush (15). We had done some work with Type V compounds earlier (5) and these were attractive candidates.

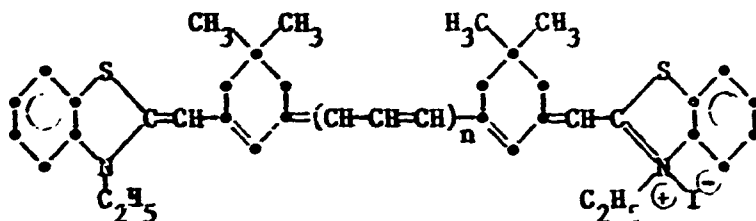
The biferrocenes Type VI, were reported by Kaufman and Cowan (16). Biferrocene picrate (structure VIII) had broad near-infrared absorption over the region 1.4-2.0 μm with a maximum located at 1.85 μm ($\epsilon = 445$). Kaufman and Cowan (16) tentatively assigned this to an electron-transfer transition between the +2 and +3 Fe atoms in the mixed valence salt of oiferrocene.



X = picrate

VIII

It is well known that certain dyes which aggregate due to interactions with each other and their environment will, in the aggregate state, give rise to band splittings of the electronic absorption spectra resulting from intermolecular excitonic bands which may shift to shorter and/or longer wavelengths. In the carbocyanine dyes, Type VII, the shift to longer wavelengths (0.05 to 0.1 μ m) is found both in solution and in the solid state. In particular in the solid state, aggregation has been shown to increase the light-fastness of the dye. The compounds of this type that we considered were the 3,3'-diethyl-9,11; 15,17-dineopentylene thia-n-carbocyanine iodides (below). These compounds have been shown to have $\lambda_{\max} \sim 1.4 \mu$ m.



$$n = 1, 2, 3$$

It was hoped that in a plastic medium, the λ_{\max} could be shifted another 0.100 μ m. In addition, the literature suggests that in a plastic, the light stability could be increased.

Our initial work was to obtain from our research sample files, to purchase, or to synthesize representative examples of each of the seven types of compounds just discussed. Spectral determinations were made and the more promising candidates were examined in plastic formulations. In addition, our research files were broadly searched for other compounds which might absorb between 1.0-3.0 μ m.

In the section which follows, the terms absorptivity, a , and molar absorptivity, ϵ , are used. These are defined as follows.

The absorptivity or the a value is obtained by dividing the absorbance, A , (log to the base 10 of the reciprocal of the transmittance = $\log_{10} \frac{1}{T}$) by the product of the concentration of the substance and the sample path length.

$$a = \frac{A}{bc}$$

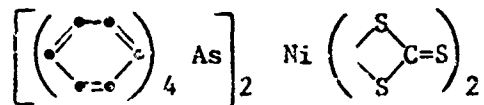
where b is the internal cell or sample length in centimeters and c is the concentration in grams per liter.

The molar absorptivity, ϵ , is the product of the absorptivity and the molecular weight of the substance

$$\epsilon = a (\text{molecular weight}).$$

1. Type I Compounds

Bis(tetraphenylarsonium)bis(trithiocarbonate) Ni^{II}



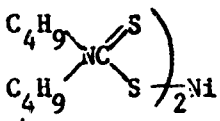
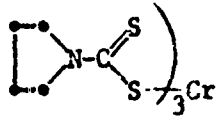
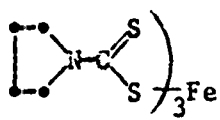
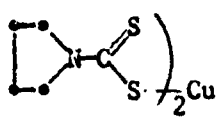
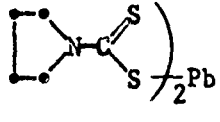
was prepared by adding a solution of dipotassium trithiocarbonate to a saturated solution of nickel acetate, and then precipitating the desired compound by adding tetraphenylarsonium chloride.

A qualitative spectral curve was determined in acetone.

λ max (μm) 0.540 (shoulder) 0.505 0.479

The compound was not evaluated in plastics, since there was no absorbance in the near-infrared region.

The following metal complexes of dichiocarbamates were prepared and preliminary spectral properties measured.

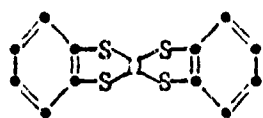
| <u>Compound</u> | <u>Color</u> | <u>Solvent</u> | <u>Absorption, μm</u> |
|--|--------------|----------------|---|
|  | Green | Acetone | 1.915; 1.415; 0.635; 0.635 |
|  | Blue | DMF | 0.645; 0.500 |
|  | Black | Acetone | 1.9; 1.42; 0.595; 0.480; 0.420 |
|  | Red-brown | Acetone | 1.9; 1.415; 0.630 (shoulder); 0.5 |
|  | White | DMF | No NIR absorptions |

The near-infrared absorption of the Ni, Fe and Cu compounds were found to be due to an interaction of the carbamate with acetone. Thus, in reality, none of the dithiocarbamates examined had any near-infrared activity.

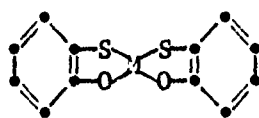
2. Type II Compounds

As discussed earlier, this structure appeared to offer considerable versatility and was investigated more broadly than the other compound types.

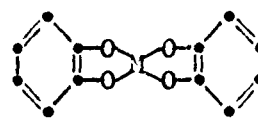
Six categories were established:



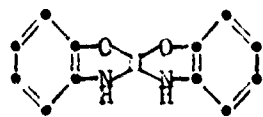
Type A



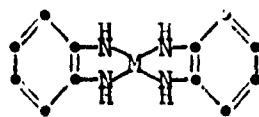
Type B



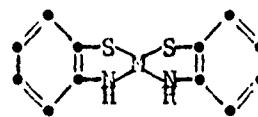
Type C



Type D



Type E



Type F

Table IV lists the Type A compounds which were investigated.

Table IV

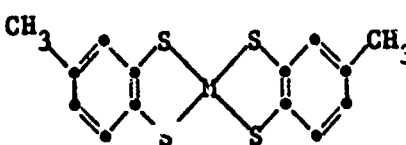
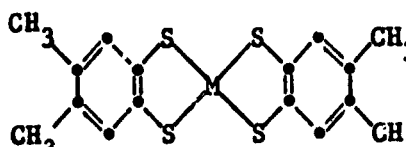
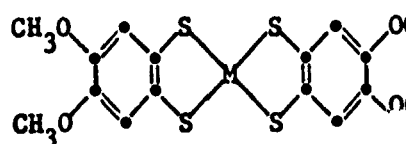
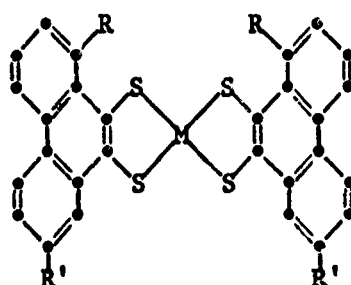
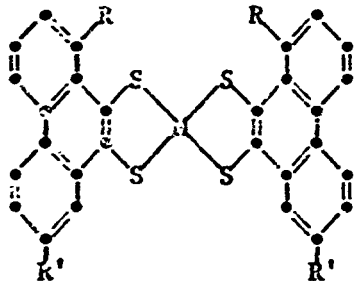
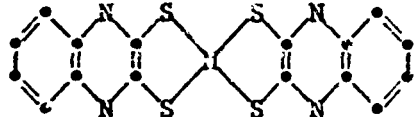
| Type A Compounds | | | | | |
|------------------|---|---|------------------------------------|-------------------|------|
| | Structure | Metal Anion | Spectral Features | | Ref. |
| | | | λ (μm) | a | |
| (1) |  | Ni^- N^+ | 0.890 | 23.4 (acetone) | (17) |
| (2) | " | Ni^- K^+ | 0.890 | ~ 23 | |
| (3) | " | Cu^{++} | 0.895, shoulder 1.1 (DMF) | | |
| (4) |  | Ni | 0.900 | | |
| (5) |  | Ni^- Bu_4N^+ | 0.950 0.740 shoulder | 46.9 | |
| (6) | " | $\text{Pt}, \text{Bu}_4\text{N}^+$ | 0.890 (CH_2Cl_2) | | |
| (7) | " | $\text{Pd}, \text{Neutral}$ | 1.3 (DMF) compound impure | | |
| (8) | " | $\text{Pd}, \text{Bu}_4\text{N}^+$ | 1.3 compound impure 0.980 (DMF) | | |
| (9) |  | Ni^- Bu_4N^+ $\text{R}=\text{R}'=\text{H}$ | 0.970 compound impure | | |

Table IV - Continued

| | Structure | Metal Anion | Spectral Features | | Ref. |
|------|---|---|-----------------------------|-----|------|
| | | | λ (μm) | a | |
| (10) |  | Ni^- Bu_4N^+ $\text{R}=\text{CH}_3$, $\text{R}'=(\text{CH}_3)_2\text{CH}$ | 0.970 | | |
| (11) |  | Ni^- Bu_4N^+ | 0.860 0.555, 0.530 | | |

In Table V, the compounds of Type B are summarized.

Table V

Type B Compounds

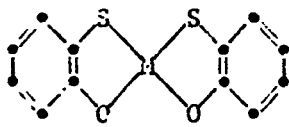
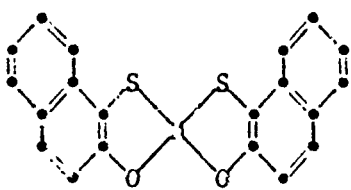
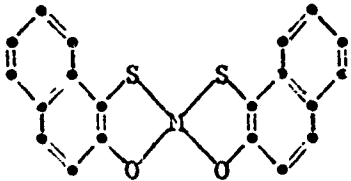
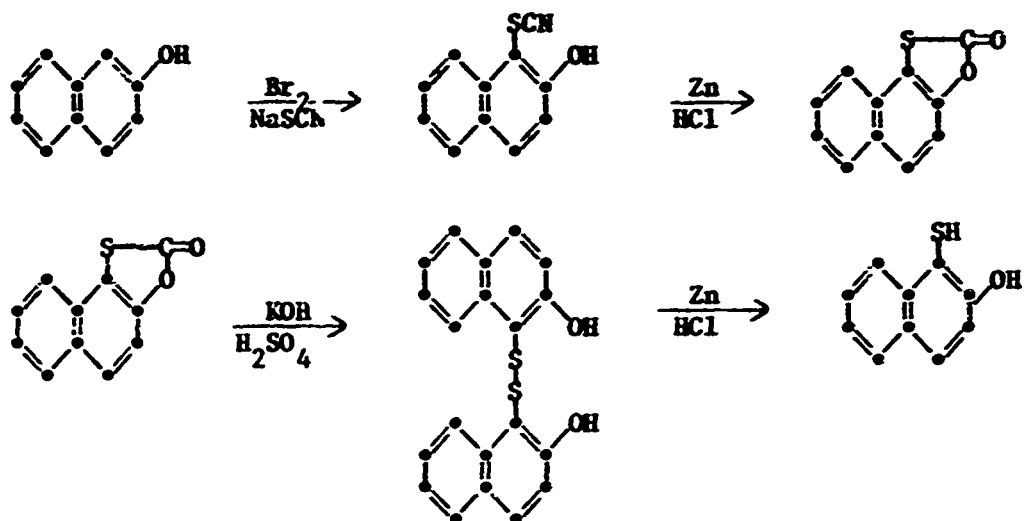
| | Structure | Metal Anion | Spectral Features | | Ref. |
|-----|---|--|---|--|------|
| | | | λ (μm) | a | |
| (1) |  | Ni^- Bu_4N^+ | 1.02 | 25.5 | (18) |
| (2) | " | Pd^- Bu_4N^+ | No complex obtained. | | |
| (3) |  | Ni^- Bu_4N^+ | 1.62 1.34 1.06 0.585 | 4.1 9.8 17.1 1.5 | (18) |
| (4) | " | Ni^- K^+ | 1.675 1.565 1.36 1.185 1.1 0.725 0.555 0.530 0.450 Compound impure | 7.5 5.8 15.9 25.5 31.3 1.3 1.8 1.8 3 | |

Table V - Continued

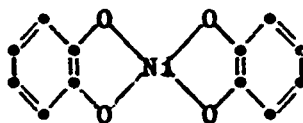
| | Structure | Metal Anion | Spectral Features | | Ref. |
|------|---|---|--|---|------|
| | | | λ (μm) | a | |
| (5) |  | Pd^- $(\text{C}_4\text{H}_9)_4\text{N}^+$ | 1.64 | | (18) |
| (6) | " | Pt^- $(\text{C}_4\text{H}_9)_4\text{N}^+$ | No NIR absorption | | (18) |
| (7) | " | Cu^- $(\text{C}_4\text{H}_9)_4\text{N}^+$ | No NIR absorption | | (18) |
| (8) | " | Ni^- Cu^{++} | Absorption spectra similar to compound (3) | | |
| (9) | " | Ni Neutral | 1.08 | | |
| (10) | " | Ni^- Genacryl Blue | 1.02 0.635 | 15.7 Curve too strong to measure "a" | |
| (11) | " | Ni^- $(\text{CH}_3)_3\text{S}^+$ | 0.415 Not stable | 10.4 | |
| (12) | " | Co^- Bu_4N^+ | No NIR absorption | | |
| (13) | " | Co^- K^+ | No NIR absorption | | |

Compounds 3-13 were prepared employing the ligand 1-mercapto-2-naphthol [obtained by the procedure described by Stevenson and Smiles (19)].



The complexes were prepared by the method of Balch (18, 20).

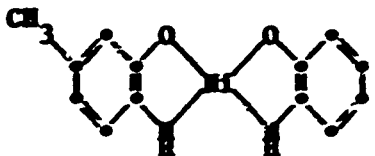
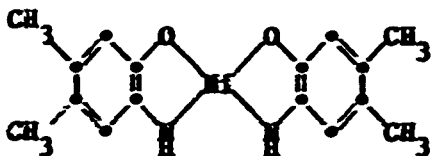
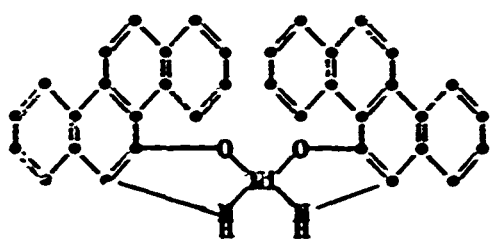
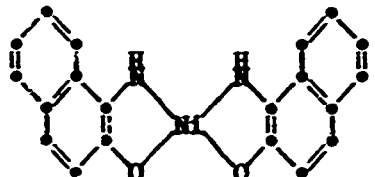
The only Type C compound obtained was:



This neutral species was black and insoluble. Thus, no spectral properties were determined.

Table VI lists the few examples of Type D compounds which were examined.

Table VI
Type D Compounds

| <u>Structure</u> | <u>Spectral Features</u> |
|---|--|
| (1)  | No NIR absorption. |
| (2)  | 0.425 μ m (strong) 0.810 μ m (strong) Too dark in visible region. |
| (3)  | 0.770 μ m, structure uncertain |
| (4)  | No NIR absorption. |

In Table VII, compounds of Type E are summarized.

Table VII
Type E Structures

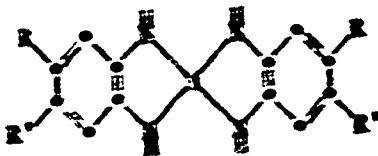
| Structure | Metal Anion | Spectral Features | | Ref. |
|---|----------------------------------|-------------------------------------|-------------------------|------|
| | | λ (nm) | ϵ | |
| (1)  | Ni R=R'=H | 0.760 | 200 (THF) | |
| | | 0.620 shoulder | | |
| | | 0.790 ($\epsilon=54,900$) | Lit. Values | (21) |
| | | 0.650 ($\epsilon=5,640$) | " | " |
| | | 0.560 ($\epsilon=2,140$ shoulder) | | |
| | | | Lit. Values | |
| | | 0.520 ($\epsilon=1,560$) | " | " |
| | | 0.420 ($\epsilon=1,260$) | " | " |
| | | 0.400 ($\epsilon=1,160$) | " | " |
| | | | | |
| (2) | Co R=R'=H | 1.135 | 10.3 | (21) |
| | | 0.765 | 48.2 | |
| | | 0.584 | 90.0 | |
| | | 1.135 ($\epsilon=3,840$) | Lit. Values | (21) |
| | | 0.763 ($\epsilon=11,700$) | " | " |
| | | 0.588 ($\epsilon=17,700$) | " | " |
| | | 0.420 ($\epsilon=2,730$) | " | " |
| (3) | Pd | 0.780 ($\epsilon=48,200$) | Lit. Values | (21) |
| | | 0.621 ($\epsilon=1,700$) | " | " |
| | | 0.568 ($\epsilon=1,280$) | " | " |
| | | 0.511 ($\epsilon=1,130$) | " | " |
| | | 0.458 ($\epsilon=924$) | " | " |
| (4) | Pt | 0.782 ($\epsilon=3,310$) | Lit. Values | (21) |
| | | 0.750 ($\epsilon=8,950$ shoulder) | | |
| | | | Lit. Values | |
| | | 0.711 ($\epsilon=96,700$) | " | " |
| | | 0.695 ($\epsilon=69,900$) | " | " |
| | | 0.680 ($\epsilon=52,200$ shoulder) | | |
| | | | Lit. Values | |
| | | 0.650 ($\epsilon=12,900$ shoulder) | | |
| | | | Lit. Values | |
| | | 0.597 ($\epsilon=3,270$) | " | " |
| (5) | Ni R=OCH ₃ R'=H | 1.0 | 44 (CHCl ₃) | |
| | | 0.520 shoulder | | |
| (6) | Ni R=CH ₃ R'=H | 0.785 (THF) | | |
| | | 0.620 shoulder | | |
| | | | | |
| | | | | |

Table VII - Continued

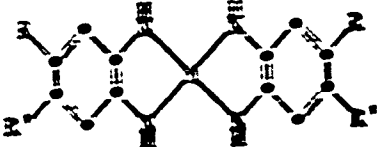
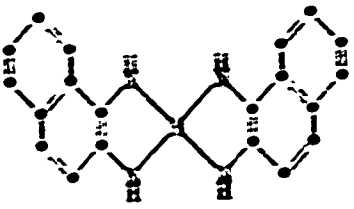

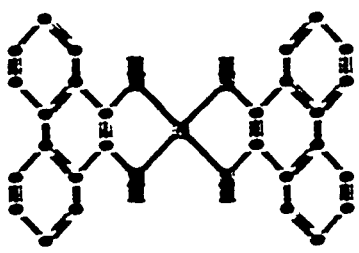
| | <u>Structure</u> | <u>Metal Anion</u> | <u>Spectral Features</u> | | <u>Ref.</u> |
|------|---|--------------------|--|------------------------------|-------------|
| | | | <u>λ (nm)</u> | <u>ϵ</u> | |
| (7) |  | Ni $R=R'=CH_3$ | 6.790 (DMF) 0.520 weak | | |
| (8) | " | Ni $R=R'=OCH_3$ | 1.02 0.54 weak 0.41 weak | | |
| (9) | " | Pt $R=R'=OCH_3$ | 0.89 | | |
| (10) | " | Co $R=R'=OCH_3$ | Unstable in solution Blue-black color | | |
| (11) | " | Pd $R=R'=OCH_3$ | 1.08 (alcohol) 0.4 | | |
| (12) |  | Ni | Strong visible absorption 1.03 (DMF) 0.855 " 0.525 " 1.0 (acetone) 0.525 " 0.420 " | | |
| (13) |  | Ni | Complex did not form | | |

Table VII - Continued

| | <u>Structure</u> | <u>Metal Anion</u> | <u>Spectral Features</u> | | <u>Ref.</u> |
|------|---|--------------------|--|--|-------------|
| | | | λ (nm) | | |
| (14) |  | Ni | 1.150 (DMF) 0.535 (DMF) | | |
| (15) | " | Pd | 1.100 (DMF) 0.425 (DMF) | | |
| (16) | " | Co | 0.775 Strong visible absorption 0.630 | | |

Compounds of Type \bar{r} are listed in Table VIII.

Table VIII

Type F Compounds

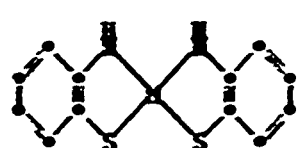
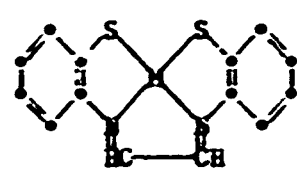
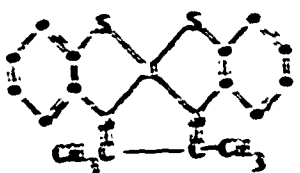
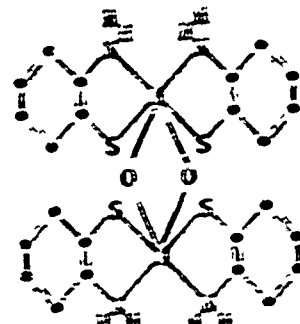
| | <u>Structure</u> | <u>Metal Anion</u> | <u>Spectral Features</u> | | <u>Ref.</u> |
|-----|---|--------------------|--|---------------------------------|-------------|
| | | | λ (nm) | ϵ | |
| (1) |  | Ni | 0.865 0.660 0.815 ($\epsilon=77,000$) Lit. Value | 95.9 (acetone) 7.2 (acetone) | |
| (2) | " | Co | 0.770 0.650 | 10.4 (DMF) 10.8 (DMF) | |
| (3) | " | Pd | 0.865 | 8.1 | |
| (4) |  | Ni | 1.030 0.810 dark red Strong visible absorption | | (22) |
| (5) | " | Co | Black, requires purification | | |

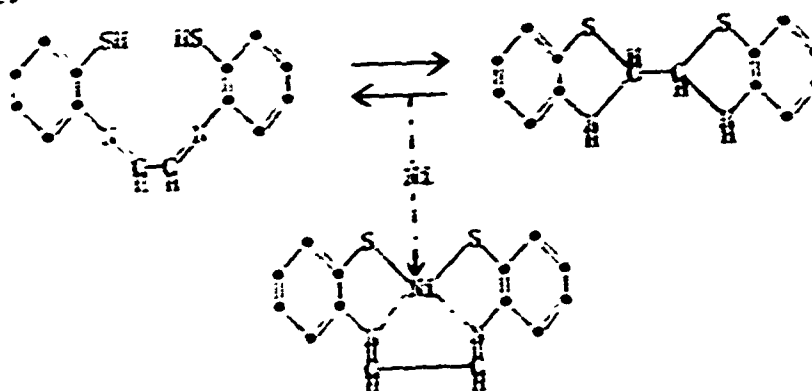
Table VIII - Continued

| Structure | Metal Anion | Spectral Features | | Ref. |
|--|-------------|----------------------|---------------------------|------|
| | | λ (m μ) | ϵ | |
| (6)  | Si | 0.950 | Strong visible absorption | |
| (7)  | Si | 0.315 | 120 (acetone) (23) | |

Compounds 1 and 7 probably identical - and structure (1) is correct.

The 1-mercapto-2-aminonaphthalene utilized to prepare compounds (1) to (3) was made from 1-naphthylamine and sulfur monochloride.

Compound (4) was made by the following procedure (22) via the bisbenz-thiazoline.



3. Type III Compounds

These structures are related to the Type II compounds. Table IX presents the compounds which were studied having the general structural features of this series.

Table IX
Type III Compounds

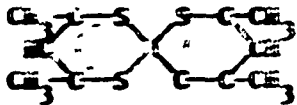
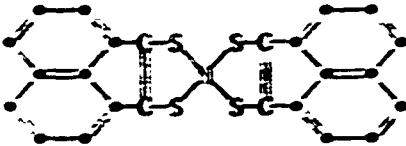
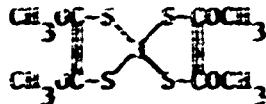
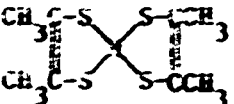
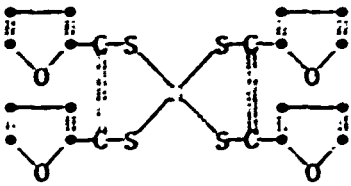
| (1) | Structure | Metal Anion | Spectral Features | | Ref. |
|-----|---|-------------|---|------------|------|
| | | | λ (μ m) | ϵ | |
| (1) |  | Co | 1.500 weak 0.900 weak | | |
| (2) | " | Ni | No NIR absorption | | |
| (3) | " | Pd | No NIR absorption | | |
| (4) |  | Ni | 1.150 (benzene) 0.900 (DMF) | | |
| (5) |  | Ni | No NIR absorption | | |
| (6) |  | Ni | 0.773 ($\epsilon=19,600$) Lit. Value (24) | | |
| (7) | " | Pt | 0.740 ($\epsilon=36,800$) Lit. Value (24) | | |
| (8) |  | Ni | 0.960 0.400-0.500 (acetone) | 0.32 | |
| (9) | " | Co | No NIR absorption Black solid | | |

Table IX - Continued

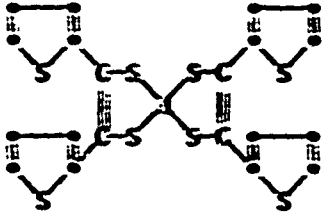
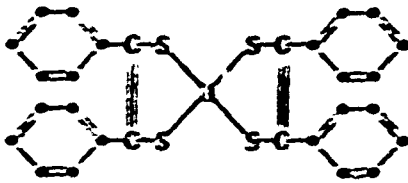
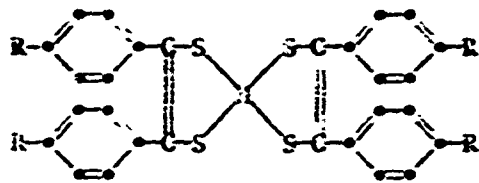
| | <u>Structure</u> | <u>Metal Anion</u> | <u>Spectral Features</u> | | <u>Ref.</u> |
|------|---|--------------------------|---|---|-------------|
| | | | <u>λ (nm)</u> | <u>ϵ</u> | |
| (10) |  | Ni | 0.970 | ($\epsilon=24,600$) Lit. Value | (24) |
| (11) |  | Co | 0.790 0.580 | (o-dichlorobenzene) (shoulder) | (25) |
| (12) | " | Ni | 0.900 0.865 | ($\epsilon=29,600$) Lit. Value | (24) |
| (13) | " | Os | 0.780 (weak) 0.570 0.550 (shoulder) | | |
| (14) | " | Pd | 0.885 | ($\epsilon=39,700$) Lit. Value | (24) |
| (15) | " | Pt | 0.800 | ($\epsilon=51,600$) Lit. Value | |
| (16) |  | Co R=OCH ₃ | 0.740 0.620 | (CHCl ₃) (shoulder) | |
| (17) | " | Pt R=OCH ₃ | 0.863 0.850 | ($\epsilon=41,600$) Lit. Value Good window in visible | (24) |
| (18) | " | W R=OCH ₃ | No NIR absorption (DMF) Black solid | | |
| (19) | " | Ni R=OCH ₃ | 0.920 (weak) | | |
| (20) | " | Ni R=OCH ₃ | 0.920 0.927 | ($\epsilon=35,600$) Lit. Value Good window in visible. | (24) |
| (21) | " | Pd R=OCH ₃ | 0.948 | ($\epsilon=37,900$) Lit. Value | (24) |

Table IX - continued

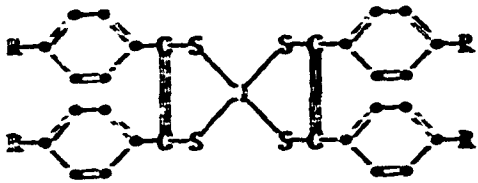
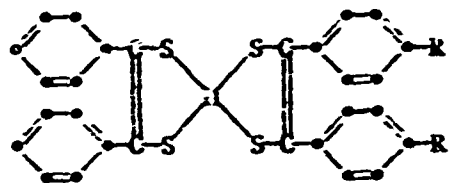
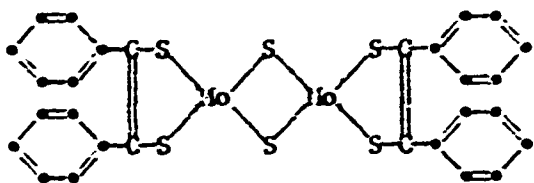
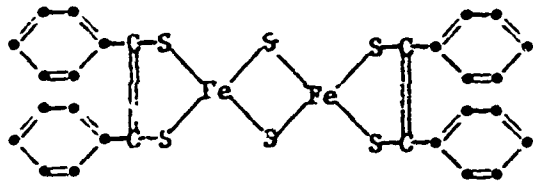
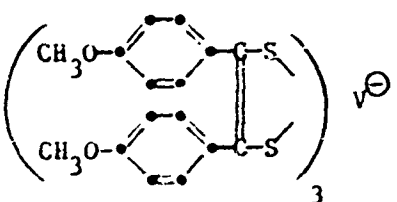
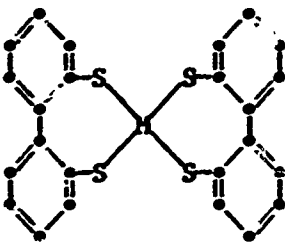
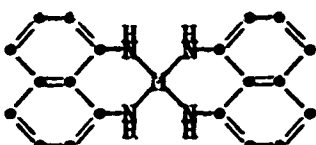
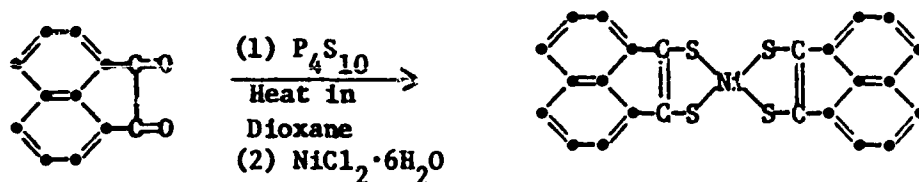
| | <u>Structure</u> | <u>Metal Anion</u> | <u>Spectral Features</u> | | <u>Ref.</u> |
|------|---|--------------------------------------|--|------------------------------|-----------------|
| | | | <u>λ (μm)</u> | <u>ϵ</u> | |
| (22) |  | Ni $R = \text{OC}_4\text{H}_9$ | 0.930 | ($\epsilon=35,600$) | Lit. Value (24) |
| (23) | " | Pt $R = \text{CH}_3$ | 0.850 | good window in visible | |
| (24) | " | Pt $R = \text{CH}(\text{CH}_3)_2$ | 0.828 | ($\epsilon=49,200$) | Lit. Value (24) |
| (25) |  | Ni $R = \text{OCH}_3$ | 0.895 | ($\epsilon=28,400$) | Lit. Value (24) |
| (26) | " | Pt $R = \text{CH}_3$ | 0.838 | ($\epsilon=42,200$) | Lit. Value (24) |
| (27) |  | | Broad absorption to 1.000 μm | | |
| (28) |  | | Absorption in visible region | | |
| (29) |  | | 0.800 0.680 | | |

Table IX - Continued

| | <u>Structure</u> | <u>Metal Anion</u> | <u>Spectral Features</u> | | <u>Ref.</u> |
|------|---|--------------------|--|-----------------------|-------------|
| | | | <u>λ (μm)</u> | <u>a</u> | |
| (30) |  | Ni | 0.705 0.530 | | |
| (31) |  | Ni | No NIR absorption | | |

Compounds 1 to 3 were prepared by bubbling H_2S through a methanolic HCl solution of acetylacetone and the appropriate transition metal halide.

Compound 4 was made as follows:



4. Type IV Compounds

The pentachlorocuprate complex of ruthenium, $\text{Ru}^{\text{III}}(\text{NH}_3)_6\text{Cu}^{\text{II}}\text{Cl}_5$, was prepared as an example of this class from hexa-ammine ruthenium trichloride and cupric chloride dihydrate. The solid which was obtained was insoluble in organic solvents, so no further work was done with it.

5. Type V Compounds

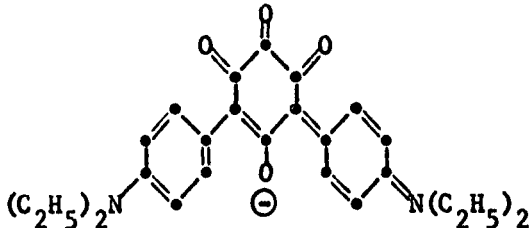
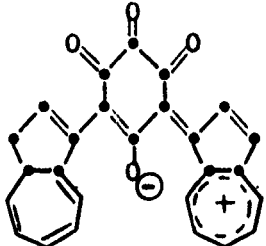
In earlier work (5) the squaric acid system provided some species with absorption in the near infrared region. The compounds investigated during the current study are listed in Table X. The aluminum, cobalt, copper and zinc salts of squaric acid had no near infrared absorption.

Table X

Squaric Acid Type Compounds

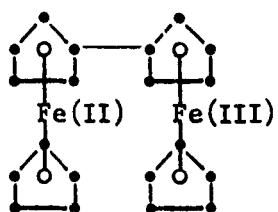
| | <u>Structure</u> | <u>Spectral Features</u> | | <u>Comments</u> |
|-----|------------------|--|-----------------------|-----------------|
| | | <u>λ (μm)</u> | <u>a</u> | |
| (1) | | 0.690 0.450 | 225 16.2 | |
| (2) | | 0.835 0.425 (DMF) | 15.1 20.8 | |
| (3) | | 0.940 0.530 (DMF) | | Unstable |
| (4) | | 0.705 (DMF) | 110.4 | |

Table X - Continued

| <u>Structure</u> | <u>Spectral Features</u> | | <u>Comments</u> |
|---|--|----------|---------------------------|
| | <u>λ (μm)</u> | <u>a</u> | |
| (5)  | No NIR absorption | | Rhodizonic acid compounds |
| (6)  | No NIR absorption | | Rhodizonic acid compounds |

6. Type VI Compounds

Biferrocenium hexafluoroantimonate,

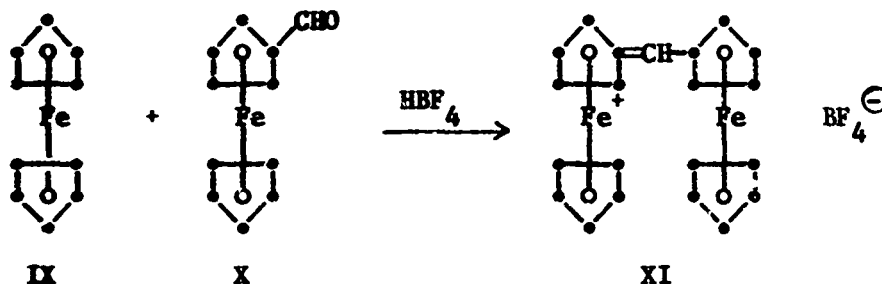


SbF_6^- , was prepared by the oxidation of

biferrocenyl with AgSbF_6 . Ullman coupling of iodoferrocene had given the biferrocenyl. The spectral curve of this compound was determined in acetone:

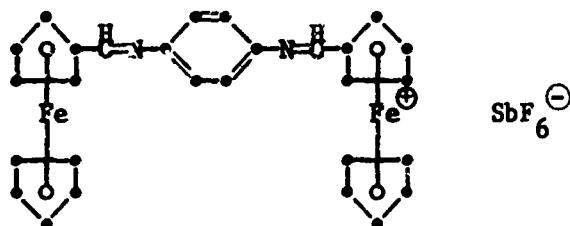
| | | |
|----------------|----------------------------------|---------------------------------|
| λ max: | $\frac{1.850 \mu\text{m}}{0.82}$ | $\frac{0.525 \mu\text{m}}{2.5}$ |
| a: | | |

Ferrocene (IX) and ferrocene carboxaldehyde (X) were condensed to give the ferrocene cyanine dye (XI). The spectral curve of XI in chloroform gave λ_{max} at 0.613 μm and 0.340 μm . There was no NIR absorption.



An attempt was made to condense ferrocene with squaric acid; however, this reaction was unsuccessful.

The Schiff base of ferrocene carboxaldehyde and p-phenylenediamine was prepared and oxidized with silver hexafluoroantimonate. The oxidation product showed no NIR absorption.



Prussian blue (ferric ferrocyanide) was prepared from FeCl_3 and $\text{K}_4\text{Fe}(\text{CN})_6$. The spectral curve (in water) showed λ_{max} at 0.710 μm .

7. Type VII Compounds

Carbocyanine dyes (azo-methine compounds), Type VII structures, were incorporated into cellulose propionate. All lost considerable absorption on FOM exposure, with or without stabilizers. Based on this light stability data, further work on these systems was not undertaken.

8. Miscellaneous Compounds

The following compounds (Table XI), were screened in attempts to find absorbers for the region 1.0-2.5 μm . The compounds were from our research files.

Table XI

Miscellaneous Compounds

| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in μm)</u> |
|--|--|
| 1. Triethylphosphonoacetate | 2.3-2.5, 1.7, 1.95 |
| 2. Cystine | None of interest |
| 3. Azulene | None of interest |
| 4. 2-Methyl indoline | 2.3-2.5, 2.15, 2.0, 1.7, 1.5 |
| 5. 2-Methylene-1,3,3-trimethylindoline | 2.3-2.5, 2.15, 2.1, 1.7, 1.625 |
| 6. 9,10-Dimethylanthracene | None of interest |
| 7. Tripropyl amine borate | None of interest |
| 8. Phenol, 3-chloromethyl, 2,4-dimethyl-5-t-butyl | 2.3-2.5, 2.1, 1.7, 1.41 |
| 9. 4,4'-Dichlorophenyl sulfone | 2.45, 2.14 |
| 10. 4,4'-Di(N-methylaminophenyl)sulfone | None of interest |
| 11. 2-Norbananol | 2.4-2.5, 2.3, 2.29, 1.7, 1.41 |
| 12. Chloroform | Several sharp peaks: 2.3-2.4, 2.1, 2.05, 1.85, 1.7, 1.4, 1.15 |
| 13. Biphenyl-3-(2-biphenyl)-5-phenyl | None of interest |
| 14. Sorbitol, 1,4:3,6-dianhydro | None of interest |
| 15. Hydrofuran, tetracarboxylic dianhydride | None of interest |
| 16. Tetracyanoethyl oxamide | None of interest |
| 17. Cyclopentadecanone | 2.3-2.5, 1.7-1.75 |
| 18. 1,5-Cyclo octadiene | 2.3-2.5 |
| 19. 1,5,9-Cyclododecatriene | 2.3-2.5, 2.1-2.2, 1.7-1.8 |

Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in μm)</u> |
|--|--|
| 20. Cyclool | 2.3-2.5, 2.05-2.15, 1.85-1.725, 1.0-2.5 |
| 21. Tetrachloro o-benzoquinone | None of interest |
| 22. Di-isodecylphthalate | 2.3-2.5, 2.15, 1.7 |
| 23. 1,4,5,8-Tetrahydroxy anthraquinone | None of interest |
| 24. N-ethyl N', n-butyl-1, 1'-azobis formamide | None of interest |
| 25. Hexachlorophene | Too weak; none of interest |
| 26. Triphenylphosphine oxide | 2.46, 2.16, 1.68 |
| 27. Tricresylphosphate | 2.3-2.5, 2.15, 1.65-1.75 |
| 28. Elastex 81P, Allied Chemical | 2.3-2.5, 2.15, 1.72, 1.76, 1.4, 1.2 |
| 29. Elastex 61P, Allied Chemical | Similar to above |
| 30. KP140, Tri(butoxy ethyl)phosphate | 2.3-2.5, 1.7-1.8, 1.4-1.2 |
| 31. Di-isodecylphthalate | None of interest |
| 32. Flexol EPO | None of interest |
| 33. Paraplex G-62 | None of interest |
| 34. p-Phenyl phenol | None of interest |
| 35. Tetrachlorohydroquinone | None of interest |
| 36. 1,3,5-Tris(2-hydroxy ethyl)-isocyanurate | None of interest |
| 37. Tetrahydrofuran | Good absorption in this region |
| 38. Hydroquinone | None of interest |
| 39. Dithio-oxamide | None of interest |
| 40. Methanol | Good absorption in this region |

Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics (Wavelength in μm)</u> |
|--|---|
| 41. 2-Phenyl triphenylene | 2.25-2.5, 1.7 |
| 42. Carbazole | 2.25-2.5, 1.7 |
| 43. Anthracene | 2.25-2.5, 1.7 |
| 44. Tetra(2-ethyl hexyl)ortho silicate | 2.25-2.5, 1.62, 1.8, 1.4, 1.2 |
| 45. SK-96-1000, G.E. Silicone | None of interest |
| 46. Iyzor TE organic titanate | None of interest |
| 47. Phenazine | None of interest |
| 48. 5-Chloro[1-H]indazole | None of interest |
| 49. 2,2'-Vinylene-pyridine | None of interest |
| 50. 1,2,4,10b-Tetrahydrofluoranthene | Weak; not of interest |
| 51. Benzonaphthofuran | Weak; not of interest |
| 52. Melamine N ² ,N ⁴ ,N ⁶ -tri-1-adamantyl | Weak; not of interest |
| 53. 1,1'-Biadamantane | Weak; not of interest |
| 54. 1, Adamantanol | Weak; not of interest |
| 55. Melamine N ² ,N ⁴ ,N ⁶ -tri-dl-endo-2-norbornyl | Weak; not of interest |
| 56. Tris[3,5-t-butyl)4-hydroxybenzyl]-phosphine oxide | Weak; not of interest |
| 57. Bis(triphenylphosphine) nickel bromide | None of interest |
| 58. Triphenylbutylphosphonium triphenylphosphine tribromonickelate | None of interest |
| 59. 2-Methylthiobenzothiazole | 2.3-2.5, 1.7, weak |
| 60. Dicyclohexylcarbodiimide | 2.3-2.5, 1.72, 1.75, weak |

Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics (Wavelength in μm)</u> |
|---|---|
| 61. Triphenyl 1,2-propylene phosphonium bromide | None of interest |
| 62. Tri(chloromethyl)phosphine oxide | None of interest |
| 63. 4,7-Dichloroquinoline | None of interest; weak 2.3-2.5 |
| 64. 1,3-Diaza[4]thiapentalene dithiol | None of interest |
| 65. Fluoranthene | 2.1-2.5, 1.575 |
| 66. 3,6-Dichloropyridazine | None of interest |
| 67. Hexamethylenetetramine | Weak; broad absorption |
| 68. 1,2,3,6,7,8-Hexahydropyrene | Weak 2.3-2.5, 2.15, 1.7-1.8 |
| 69. Hexachloropropene | Weak 2.3-2.5 |
| 70. 1,3-Propanediol | 1.45, 1.7-1.8, 1.9-2.5 |
| 71. Hexamethyldisilazane | 1.525, 1.695, 1.705, 1.75, 2.1-2.5 |
| 72. Triethyleneglycol methyl ethyl acetate | 1.725, 2.15, 2.25-2.5 |
| 73. Hexamethyldisiloxane | Weak 1.19, 1.69, 1.7, 1.75, 2.29, 2.39, 2.4, 2.475 |
| 74. 1,4,5,6,7,7-Hexachlorobicyclo-2,2,1,5-heptene-2,3-dicarboximide | None of interest |
| 75. Benzofuroxane | Weak absorption |
| 76. Bis benzofuroxanesulfone | None of interest |
| 77. 1,4,5,8-Tetrahydroxyanthraquinone | Weak 1.710, weak 2.3-2.5 |
| 78. E-702 (Stauffer Chem. Co.) | 1.715, Broad abs. 2.0-2.5 |
| 79. Pyrol PCF (Stauffer Chem. Co.) | 1.725, Broad abs. 2.2-2.5 |
| 80. Hexaketocyclohexane | Weak 2.25-2.5 |

Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in μm)</u> |
|---|---|
| 81. Tetrachloroglycoluracil | Weak 2.3-2.5 |
| 82. Hexachloroethane | Weak 2.3-2.5 |
| 83. Dichloroquinazoline | Weak 2.3-2.5 |
| 84. 3,4-Dichloroaniline | 1.48, 1.97, 2.19, 2.45 |
| 85. 2,5-Dichloroaniline | No broad absorption of interest; several sharp peaks |
| 86. 3,5-Dichloroaniline | No broad absorption of interest; several sharp peaks |
| 87. 2,4,5-Trichloroaniline | No broad absorption of interest; several sharp peaks |
| 88. 2,4,6-Trichloroaniline | Weak sharp peaks |
| 89. Tris 2,3-dibromopropylphosphate | 1.7-1.71, 2.25-2.5 |
| 90. Max Polyol R0350 M44223 Hydroxyl No. 281 | Broad, weak 1.4-1.7, 2.1, 2.3-2.5 |
| 91. O,O-Diethyl n,n-bis(2-hydroxyethyl)- aminoethylphosphonate | 2.3-2.5, 1.95, 3 peaks 1.69-1.75, weak abs. 1.45-1.6 |
| 92. 1,6-Bis(di-n-butylstanna-)2,5,7,10- tetrakisoxocyclodecane | Weak; none of interest |
| 93. Triethylamine borate | None of interest |
| 94. Magnesium silicate | None of interest |
| 95. Hexabromomethylbenzene | None of interest |
| 96. 1,6-Dibutylbiurea | None of interest |
| 97. Nickel salt of 3,5-di-t-butyl-4- hydroxy benzoic acid | No NIR absorption |
| 98. Cobalt salt of 3,5-di-t-butyl-4- hydroxy benzoic acid | Extremely insoluble but showed some broad absorption with the λ max at 1.91, 1.415, 1.18, 0.685 |

Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in μm)</u> |
|--|--|
| 99. Copper complex of salicylaldehyde-ethylene diamine | Showed near-infrared absorption (weak) with λ max at 1.9, 1.14 and 0.585. A sample was submitted for testing in plastic. |
| 100. Ruthenium dichloridetriphenyl phosphine complex | Very broad NIR absorption. Sample submitted for testing in plastic. |
| 101. 2',6-Cyclo octatriene-1-one | None of interest |
| 102. 2(1H)-Pyridine-5,6'-dichloro-1,1'-oxalyl di | 2.1-2.5, 1.9-2.0, 1.65-1.75, 1.4, 1.15-1.185 |
| 103. 1,2-Dithiolium iodide-3 (or 5)-methyl-thio-4-phenyl | 2.2-2.5 |
| 104. Iodonium bromide, diphenyl | 2.2-2.5 |
| 105. Acrylophenone, 3,3'-dimercapto-4-dimethylamino | 2.3-2.5 |
| 106. Acetamide, 2,2'-(vinylene dithio)bis-cis | 2.3-2.5 |
| 107. Butyranilide-2,3-dioxo-2,3-dioxime | Weak 2.3-2.5 |
| 108. Butyranilide-2,3-dioxo-3-methyl phenyl hydrazone-2-oxime | None of interest |
| 109. 1,2-Dithiolium hydrogen sulfate, 4-phenyl | None of interest |
| 110. Thiopyrylium fluoborate (BF_4^-)-2,4,6-triphenyl | None of interest |
| 111. Naphtho-(2,1,b)thiophene-1,2-dione | None of interest |
| 112. 4-Hydroxypteridine | None of interest |
| 113. 9-Methyl-2,3,7-trihydroxy-6-fluorone | Very insoluble; no NIR absorption of interest |
| 114. 1,2-Dithiolium sulfate (HSO_4^-)-4-p-nitrophenyl | None of interest |

Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in nm)</u> |
|---|--|
| 115. 1,2-Bis(thiolium-4-sulfate-5- (p-dimethylaminophenyl) | None of interest |
| 116. 3H-1,2-Benzodithiole-3-thione | None of interest |
| 117. Tetrachlorothiophene | None of interest |
| 118. 3H-1,2-Dithiole-3-thione-5- (p-dimethylaminophenyl) | None of interest |
| 119. 2-Mercaptothiazoline | None of interest |
| 120. 2-Mercaptobenzimidazole | None of interest |
| 121. 2-Mercaptopyrimidine | None of interest |
| 122. Pentachloropyridine | None of interest |
| 123. Naphtho-(1,8,cd)-1,2-diselenoli- hexachloro | None of interest |
| 124. 3H-1,2-Benzothiaselenol-3-one | None of interest |
| 125. 3H-1,2-Benzothiaselenol-3-thione | None of interest |
| 126. Pyrazole, 3,5-dimethyl-4-nitroso- 1-phenyl | None of interest |
| 127. 1,3,5-Trioxa-2-sila-4,6-diborine- 2,2,4,6-tetraphenyl | None of interest |
| 128. Isothiazole-4-phenyl-1,1,2-trioxide | None of interest |
| 129. 4H-1,2-Diazepine-3,5,7-triphenyl | None of interest |
| 130. Sydnone-3-(3-pyridyl), methiodide | 2.35-2.5, 1.725 |
| 131. 1,3,2-Dithiarsolium iodide, 4,5-dicyano | 2.35-2.5, 1.725 |
| 132. 1,3,2-Dioxaborinide-2,2-difluoro- 4-methyl-6-phenyl | 2.35-2.5, 1.725 |
| 133. Pyrazolium perchlorate-1,2,4- triphenyl | None of interest |

Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in mμ)</u> |
|---|--|
| 134. Ethanol-1,1'-dithiobis(2,2,2-trichloro) | None of interest |
| 135. Butarethiol, copper | Insoluble |
| 136. Phenol-2,4,5-trichloro carbamate | 2.0-2.5, 1.965, 1.65-1.75, 1.4, 1.175; decomposed on irradiation |
| 137. 3-Methylene-2-norbornanone | None of interest |
| 138. 1,6-Heptadiene-3,5-dione-1,7-bis-p-dimethyl aminophenyl | None of interest |
| 139. 1,2,3-Propane trione-1,3-diphenyl-2-oxime | None of interest |
| 140. 4,7-Methanoinden-5-(4H)-one, 3a,6,7,7a-tetrahydro | None of interest |
| 141. Sulfonium iodide(4,5-diphenyl-1,2-dithiol-3-ylidene)methyl | None of interest |
| 142. Dithiane | None of interest |
| 143. Pyrazolium-p-toluenesulfonate, 1,2-dimethyl-4-phenyl | None of interest |
| 144. 4H-1,2-Diazepine-3,5,7-dimethylamino | None of interest |
| 145. (2H)-Naphthalenone-2,2'-1,2,4-trithiolane-3,5-diylidine)bis-(3,4-dihydro-4-methyl) | None of interest |
| 146. 3H-1,2-Benzodithiole Δ^3 - α -malono-nitrile | None of interest |
| 147. 2H-Benzotriazole-4,5,6-trimethoxy-2-phenyl | None of interest |
| 148. 2H-1,2,3-Triazole-4-carboxanilide-5-methyl-2-phenyl | None of interest |
| 149. Ammonium iodide, ethyl dimethyl (3-oxo-3H-1,2,4-dithiazol-5-yl) | None of interest |

Table XI - Continued


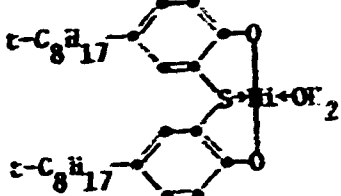
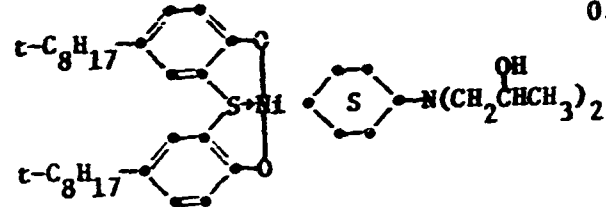
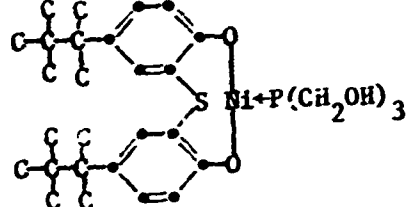
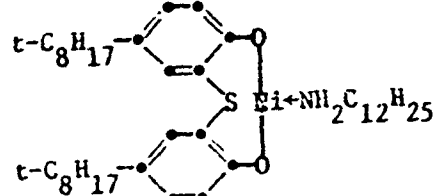
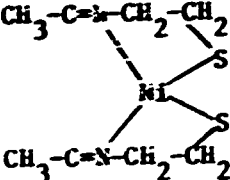
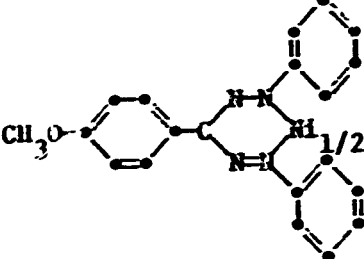
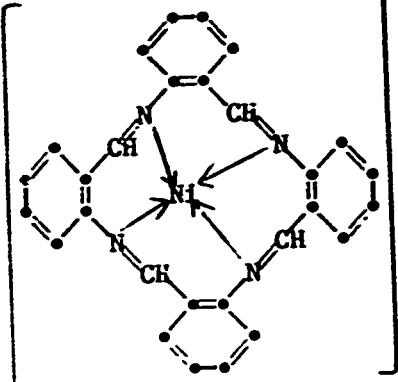
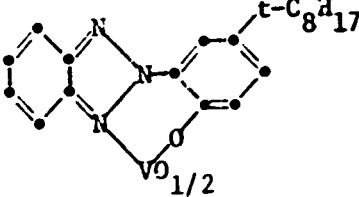
| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in mμ)</u> |
|---|--|
| 150. 1,3-Isindione-2-(3-methyl-2-benzothiazolinylidene) | None of interest |
| 151. Nickel complex of salicylaldehyde-ethylenediamine | No NIR absorption |
| 152. Rhodium chloride-triphenyl phosphine complex | No NIR absorption |
| 153. $(C_2H_5O)_2P-NH-SH-P(OC_2H_5)_2$  | 0.80 |
| 154.  | 1.18 (weak) (DMF) |
| 155.  | 1.1 (CHCl ₃) 0.665 (weak) |
| 156.  | 1.1 (CHCl ₃) 0.68 (weak) |
| 157.  | 1.1 (CHCl ₃) 0.64 (weak) |

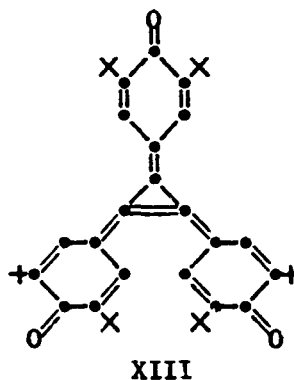
Table XI - Continued

| <u>Name</u> | <u>Absorption Characteristics</u> <u>(Wavelength in μm)</u> |
|--|--|
| 158. $(\text{C}_8\text{H}_{17})_2\text{PS}_2\text{Ni}_{1/2}$ | 0.73 (CHCl_3) 0.56 |
| 159.  | 6.81 (shoulder, weak) 0.54 (CHCl_3) |
| 160.  | 0.8 (CHCl_3) 0.45 (strong) |
| 161.  | 0.7 (CHCl_3) 0.5 |
| 162.  | 0.76 (CHCl_3) |
| 163. Acryloid AT-56 resin | 2.3 |
| 164. Glycerin | 2.05-2.5 |

Evaluations of these compounds which had NIX absorption are further discussed in Section B, Evaluations With Plastics.

Tri(3,5-di-t-butylquino)cyclopropane (XIII), was prepared by oxidizing bis(3,5-di-t-butyl-4-hydroxyphenyl)quinocyclopropane with potassium ferricyanide. The spectral curve of the compound was determined in CHCl_3 .

| <u>λ max (μm)</u> | <u>0.770</u> | <u>0.685</u> | <u>0.625</u> | <u>0.390</u> |
|--|--------------|--------------|--------------|--------------|
| a | 60.2 | 60.2 | 34.7 | 52.9 |



The compound was found to be extremely heat sensitive in a PVC mix turning from blue to yellow in color. The same behavior was noted in cellulose propionate. A dispersion showed no absorption from 0.3-2.5 μm .

A possible explanation for the color change is the transfer of energy of the singlet state of the cyclopropane to the triplet state of oxygen yielding the triplet state of the cyclopropane and the singlet state of oxygen. Singlet oxygen is a dienophile and could add across one or more of the double bands in the cyclopropane; thereby disrupting the conjugation of that system with the resulting change in color from blue to yellow.

B. Evaluations With Plastics

Some of the earliest work on the spectral properties of plastics is recorded in a 1955 Bulletin of the American Standards Association (now called American National Standards Institute) (26). This publication indicated that the cellulosic polymers (Figures 73-75 and 79-82 of the Bulletin) have considerable transmittance between 0.90-2.7 μm and 3.5-5.5 μm . Styrene polymers (Figures 83-86) transmit between 0.40-3.2 μm and 3.6-6.7 μm , although there are several sharp absorption bands in these regions. Polymethyl methacrylate generally transmits between 0.40-2.2 μm but has strong absorption between about 2.3-2.5 μm and 3.2-3.6 μm (Figures 87 and 91). A clear polyvinyl chloride has substantial transmission in the ranges 0.40-3.4 μm and 3.6-5.6 μm (Figure 92). Figure 93 indicates that polymonochlorotrifluoroethylene transmits broadly between 0.30 and 7.0 μm . The polyallyldiglycol carbonate polymer, CR-39 (Figures 94 and 95), has good transmittance between 0.40-2.2 μm and absorbs from 2.3-3.5 μm . Polyester-type polymers seem to have similar transmittances (Figures 97 and 98 of Reference 26).

Based on these reference curves, we have done some calculations on transmittance of some of these polymers in the region from 2.0-4.0 μm at a thickness of 125 mils. These data are shown in Table XII.

Table XII
Spectral Data For Several Plastics

| Wavelength, μm | Transmittance, % | | | |
|------------------------------|------------------|-----------------------------------|-------------------------------|-------------------|
| | PVC (Fig. 92) | Cellulose Acetate (Fig. 75) | Poly- styrene (Fig. 83) | PMMA (Fig. 88) |
| 2.000 | 43.5 | 31.6 | 60.0 | 57.0 |
| 2.100 | 11.7 | 10.6 | 7.8 | 17.7 |
| 2.200 | 0.0 | 2.1 | 27.4 | 1.0 |
| 2.300 | 0.0 | 0.0 | 2.1 | 0.0 |
| 2.400 | 2.4 | 0.0 | 0.4 | 0.0 |
| 2.500 | 3.5 | 0.0 | 0.5 | 0.0 |
| 2.600 | 2.6 | 2.6 | 3.5 | 3.0 |
| 2.700 | 1.1 | 0.0 | 2.7 | 1.0 |
| 2.800 | 0.6 | 0.0 | 3.5 | 0.0 |
| 2.900 | 0.6 | 0.0 | 7.8 | 0.0 |
| 3.000 | 0.2 | 0.0 | 9.4 | 0.0 |
| 3.100 | 0.0 | 0.0 | 1.0 | 0.0 |
| 3.200 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3.300 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3.400 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3.500 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3.600 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3.700 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3.800 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3.900 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4.000 | 0.0 | 0.0 | 0.0 | 0.0 |

Ralph Stair (27) presents other related data on plastics. Mr. Stair indicates that there is 80-90% transmittance between 0.330-0.950 μm for the following plastics: polymethyl methacrylate, polyallyldiglycol carbonate, cellulose acetate butyrate, cellulose propionate, ethyl cellulose and polystyrene.

Our data are in agreement with these literature references. The transmittance curve for a 125-mil thick polymethyl methacrylate filter is shown in Figure 3. The absorbers we used in this filter provide the 0% transmittance between 0.300-0.650 μm . Absorption between 2.2-4.1 μm is due to the plastic alone.

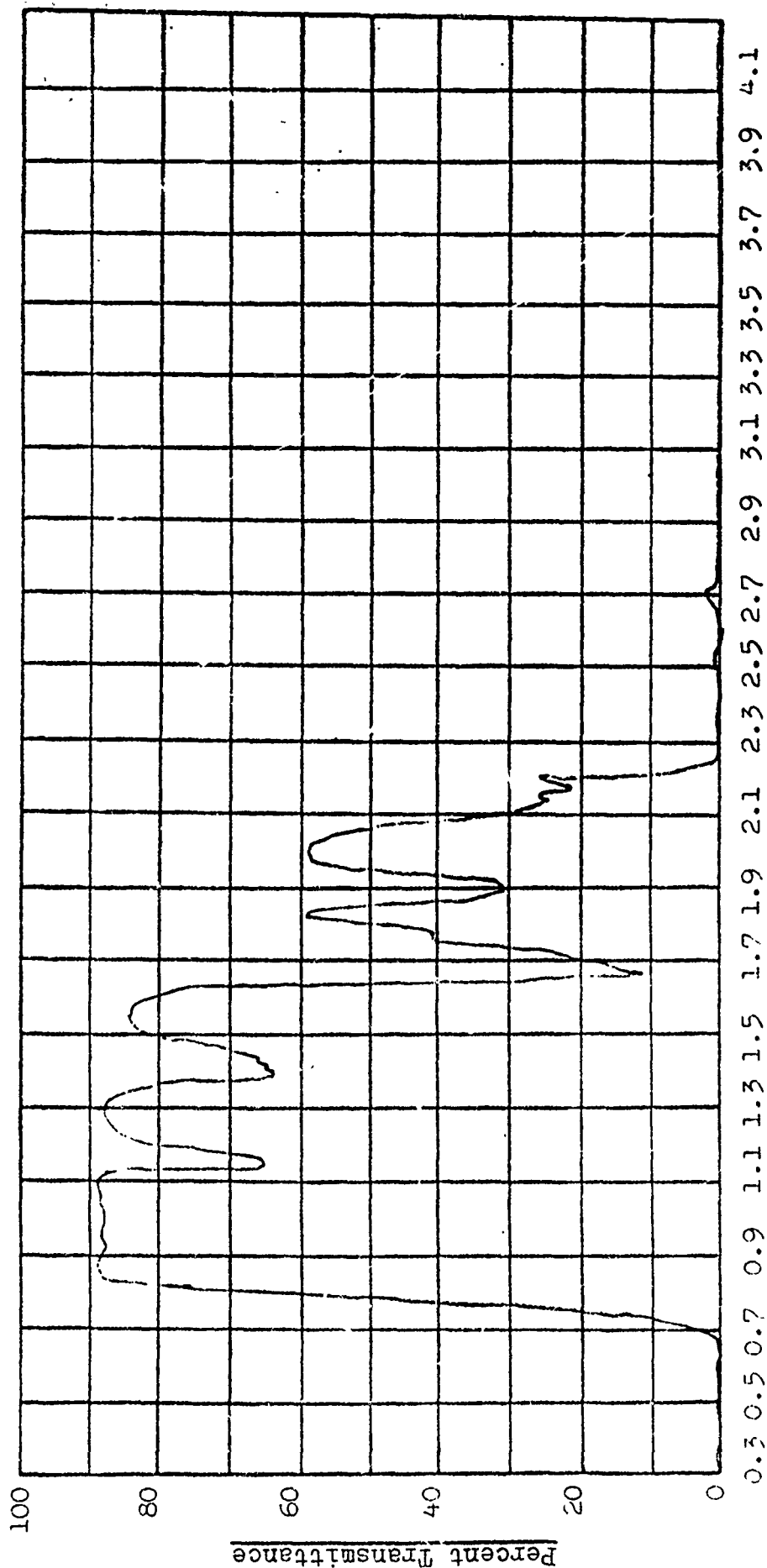
As mentioned earlier, Figure 2 is an illustration of the fact that plastic materials have transmittances between 1.8-2.2 μm and 2.4-2.5 μm that is difficult to eliminate.

(1) Plastic Absorption at 10.6 μm

We have calculated the absorption at 10.6 μm for several plastics. Thin films of the plastics were examined using a Perkin-Elmer 237B Spectrophotometer. All of the plastics had sufficient absorption to offer time/energy-dependent protection against CO_2 lasers. The PMMA appeared to have the strongest absorption at 10.6 μm , and the polycarbonate had the weakest absorption. The results are shown in the following Table XIII.

Figure 3
VISIBLY OPAQUE FILTER

R7511-2



WAVELENGTH IN MICROMETERS

Table XIII

Absorption of Plastics at CO₂ Wavelength

| <u>Film</u> | <u>Thickness (Mils)</u> | <u>10.6 μm O.D./Mil.</u> | <u>O.D. at 100 Mils</u> |
|----------------------|-----------------------------|---|-----------------------------|
| Lexan Polycarbonate | 5.5 | 0.113 | 11.3 |
| PMMA | 1.1 | ∞ | ∞ |
| Flexible PVC | 1.3 | 0.385 | 38.5 |
| Polyphenylene Oxide | 3.7 | 0.541 | 54.1 |
| Cellulose Propionate | 2.1 | 0.314 | 31.4 |

1. Cellulose Propionate

Since cellulose propionate had proven to be the polymer of choice for molded laser safety products in previous work (1-3, 6, 8), this polymer was preferentially used to study formulations in plastics.

Biferrocenium hexafluoroantimonate was evaluated in a cellulose propionate film.

10 g Cellulose propionate

0.04 g Biferrocenium hexafluoroantimonate

0.2 g CYASORB® UV 24 Light Absorber

A 4-mil film had extremely weak absorption at 1.725 μ m and 0.540 μ m. After 100 hours of FCM exposure, the sample had lost all NIR absorption.

A polymer sample with glycerin added to absorb in the 1.8 to 2.5 μ m region was hazy as the glycerin was incompatible with the polymer system.

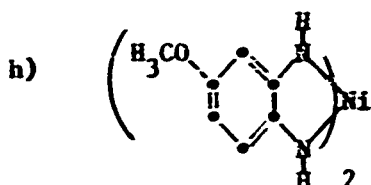
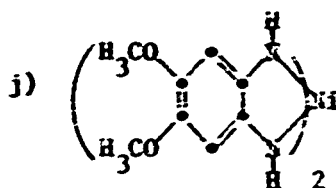
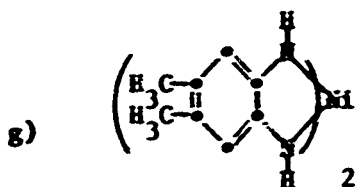
The following were injection-molded in cellulose propionate to determine their usefulness:

- a) K^+ salt of 8-naphthol mercapto Ni complex
(Decomposed on molding.)
- b) Cu^{++} salt of 8-naphthol mercapto Ni complex
(Decomposed on molding.)
- c) Cu^{++} salt of toluenedithiol Ni complex
(Decomposed on molding.)
- d) Phenanthrene diamine Ni complex
(Strong peak at 1.08 μm , but too much visible absorption.)
- e) Phenanthrene diamine Pd complex
(Peak at 1.1 μm too weak for use.)
- f) Xylene dithiolato nickel complex
(Strong absorption centered at 0.39 μm .)

Interestingly in comparing (d) and (e), the use of Pd instead of Ni gives a shift of 0.03 μm to higher wavelengths. None of these absorbers was found to be useful for the contract.

A curve of $Ni(NO_3)_2 \cdot 6H_2O$ in DMF showed very strong near-infrared absorption. An attempt was made to incorporate this into cellulose propionate to see if it would be compatible. Thus, a 2% loading of the salt was hot-roll-milled and compression-molded in cellulose propionate. However, the resulting sheets were opaque, as the salt was not compatible. A nickel acetate sample gave the same results. A 2% loading of nickel acetylacetonate was compatible and gave clear samples but had no NIR absorption.

Compounds g, h, j and k did not survive the molding conditions when incorporated into cellulose propionate.



CYASORB H-249 Infrared Absorber was molded in cellulose propionate to give a 60-mil sample with luminous transmittance of 18.5% and O.D. of 7.2 at 0.6943 μm . Too high a concentration of H-249 was used, so the O.D. was high, but calculations showed that even at an O.D. of 4.0, the material would be too dark in the visible region to be of use.

The compound obtained from the reaction of squaric acid coupled with β -naphthol was insoluble in cellulose propionate or methyl methacrylate and could not be evaluated.

A sample of $\left[\left(\text{C}_6\text{H}_4 \right)_3 \text{P} \right]_2 \text{CoCl}_2$ in cellulose propionate was

found to have very weak absorption at 0.6943 μm , thus would not be of use.

A sample of bis(dithiofurfuryl)nickel was evaluated in cellulose propionate for its absorption at 1.055 μm . However, it was extremely weak, and is not of use.

The tetrabutylammonium salt of nickel thionaphthol was evaluated in C.P., with and without hexaethylmelamine as a stabilizer. The films had fairly

broad NIR absorption. After 200 FOM hours, the films had lost considerable strength. The melamine compound appeared to hasten the degradation of the absorber in this comparison.

Thin solvent-cast films of CYASORB IR-117 Infrared Absorber and CYASORB IR-126 Infrared Absorber in cellulose propionate were prepared and were exposed in the FOM to ascertain which absorber would be best for affording broad absorption in the NIR region. The same was done with CYASORB IR-99 Infrared Absorber and CYASORB IR-282 Infrared Absorber to determine which would be best. Combinations of IR-126 or IR-117 with IR-99 and IR-282 were made with absorption in the NIR, but not with a high O.D. at 0.6943 μ m. IR-99 and IR-117 or IR-126 formulations with high O.D.'s at 0.6943 μ m and 1.06 μ m with broad NIR absorption were also prepared. The formulations had the following properties: (Y = Luminous Transmittance):

R7927-180A - IR-117 alone

R7987-180B - IR-126 alone

R7987-181A - IR-99 alone; O.D. at 1.06 μ m = 3.8, Y = 82%

R7987-181B - IR-282 alone; O.D. at 1.06 μ m = 3.9, Y = 84%

R7987-181C - IR-99 + IR-117

R7987-181D - IR-99 + IR-126

R7987-181E - IR-282 + IR-117

R7987-181F - IR-282 + IR-126

R7987-185A - IR-126 + IR-99; Y = 30%, O.D.'s 2.8 at 0.6943 μ m,
4.5+ at 1.06 μ m

R7987-185B - IR-282 + IR-126; Y = 46%, O.D. - 4.5 at 1.06 μ m

After 100 hours of FOM exposure, some of the above films were evaluated. In the IR-117 versus IR-126 series (R7987-180A and -180B), the IR-126 seemed to be more light-stable, and had a higher Y value. In the IR-99 versus IR-282 series (R7987-181A and -181B), the IR-282 appeared to be more stable again with a higher Y value. When two NIR absorbers were used together, the results were slightly different. Here, IR-99 and IR-126 were the best for light stability (R7987-181B). This appeared to be more stable than even IR-282 and IR-126 together (R7987-181F).

On sample R7987-185B, the NIR curve "bottoms" (is at 0% transmittance) from 0.780 to 1.800 μm . The curve lifts above 1.80 μm , and no absorber has been found yet which can be added to reduce this transmission.

Using the above absorbers, formulations of broad absorption products were initiated (Table XIV). First, a system with a high O.D. at 1.06 μm with broad absorption in the 1 to 6 μm range, with a low O.D. at 0.6943 μm was looked at (R8203-4B). The O.D. was at least 3.0 from 0.80 to 1.74 μm . From 1.74 μm to 2.7 μm , the sample had small transmittance peaks (maximum of 30% T) and the O.D. was 3.0 or over from 2.7 to 6.0 μm .

However, since the combination of IR-99 and IR-126 appeared to have better light stability, sample R-8203-13A was molded. The sample "bottomed" from 0.780 to 1.78 μm in the near infrared. After 500 hr of FOM exposure, the sample gives good neodymium protection with broad absorption to 1.8 μm . There was 76.4% of the broad line absorber remaining.

Samples R8203-10A, 10B and 10C were molded to obtain absorption at 0.530 μm as well as 0.6943 μm and 1.06 μm . The samples - 10A and 10B had good FOM stability through 500 hr of exposure (Table XIV). After 1,500 hr

Table XIV

Formulations in Cellulose Propionate

| <u>Sample, R3203-</u> | <u>4B</u> | <u>10A</u> | <u>10B</u> | <u>10C</u> | <u>13A</u> | <u>44A</u> | <u>44B</u> |
|---------------------------|-----------|------------|------------|------------|------------|------------|------------|
| Cellulose Propionate, g | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 |
| CYASORB IR-99, g | - | 4.55 | 6.05 | 5.06 | 0.03 | 0.03 | 4.7 |
| CYASORB IR-117, g | - | - | - | - | - | - | - |
| CYASORB IR-126, g | 1.92 | - | - | 1.92 | 1.92 | 1.92 | 1.92 |
| CYASORB IR-282, g | 0.08 | - | - | - | - | - | - |
| K-283, g | - | 3.2 | 3.2 | - | - | - | - |
| CYASORB UV 24, g | 3.00 | 2.0 | 2.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Thickness, mils | 62 | | | 62 | | | |
| Luminous Transmittance, % | 47 | 25 | 22 | 22 | 42 | 48 | 23 |
| O.D. at 0.53 μ m | - | 4.05 | 3.93 | - | - | - | |
| O.D. at 0.6943 μ m | 0.9 | 3.5 | 4.05 | 5.5 | 1.13 | 1.0 | 4.5 |
| O.D. at 1.06 μ m | 4.5 | 4.5+ | 4.5+ | 4.5+ | 4.5+ | 4.5+ | 4.5+ |
| 500 hr FOM Exposure: | | | | | | | |
| O.D. at 0.53 μ m | - | 4.05 | 3.93 | - | - | | |
| O.D. at 0.6943 μ m | - | 3.05 | 3.53 | 4.5 | 1.09 | | |
| O.D. at 1.06 μ m | - | 4.5 | 4.5 | 4.5 | 4.5+ | | |
| Transmittance, % | - | 16.5 | 14.5 | 11 | 35 | | |
| 1,500 hr FOM Exposure: | | | | | | | |
| O.D. at 0.53 μ m | - | 3.8 | 3.75 | - | - | | |
| O.D. at 0.6943 μ m | - | 2.75 | 3.2 | - | - | | |
| O.D. at 1.06 μ m | - | 4.5 | 4.5 | - | - | | |
| Transmittance, % | - | 15 | 13 | - | - | | |

of FOM exposure, the optical density at 0.6943 μm was slightly lowered. However, the samples are considered to be quite stable. Sample 10C retained 80% of the NIR absorption after 500 hr of FOM exposure.

Samples R8203-10C and -13A were remolded and labeled R8203-44A and -44B, respectively. Sample -44A "bottomed" from 0.80-1.74 μm . Sample -44B "bottomed" from 0.66-1.76 μm . These moldings were made to confirm the reproducibility of the system.

During the course of this investigation Celanese Plastics Co. informed us that they were going out of the cellulose propionate molding powder business. Thus, we began to evaluate cellulose propionates produced by other suppliers. It was determined that the polymer produced by Tennessee Eastman could be utilized (Table XV).

Table XV
Comparison of Propionates Containing IR-99 and IR-126

| | Cellulose Propionate | | | |
|----------------------------|----------------------|---------------------|----------|---------------------|
| | Eastman | | Celanese | |
| | Initial | After 300 FOM Hr | Initial | After 300 FOM Hr |
| Luminous Transmittance | 50% | 40% | 48% | 39% |
| O.D. at 0.84 μm | 4.5+ | 3.1 | 3.7 | 3.2 |
| O.D. at 1.06 μm | 4.05 | 4.5 | 4.5 | 4.5 |
| % NIR Remaining | | 89% | | 84% |

The data indicate that any of the six formulations in Table XIV can be used to give broad band laser protection.

A multi-purpose laser spectacle developed under a previous Air Force Contract (6) was reformulated to eliminate "saturation" of the dye under Q-switched ruby laser impact. CYASORB IR-290 was eliminated in the formulation and replaced with CYASORB IR-99.

1,000 g Cellulose Propionate

6.05 g CYASORB IR-99

3.2 g K-283 Absorber

2.0 g CYASORB UV 24

This had a luminous transmittance of 22% with the following O.D.'s.

| <u>λ (μm)</u> | <u>1.06</u> | <u>0.6943</u> | <u>0.671</u> | <u>0.633</u> | <u>0.530</u> | R8203-10B |
|--|-------------|---------------|--------------|--------------|--------------|-----------|
| O.D. | 4.5+ | 4.1-- | 2.7 | 1.2 | 4.0 | -- |

Another formulation with a slightly lower O.D. at 0.6943 μm was prepared.

1,000 g Cellulose Propionate

4.55 g IR-99

3.2 g K-283

2.0 g UV 24

| R8203-10A | <u>λ (μm)</u> | <u>1.06</u> | <u>0.6943</u> | <u>0.671</u> | <u>0.633</u> | <u>0.530</u> | <u>Y Value (%)</u> |
|-----------|--|-------------|---------------|--------------|--------------|--------------|--------------------|
| | O.D. | 4.5+ | 3.5 | 2.3 | 1.1 | 4.1 | 25 |

This was slightly lighter than R8203-10B.

2. Polycarbonate

Merlon M39F polycarbonate was evaluated with CYASORB IR-117 Infrared Absorber as a possible substrate by mixing 0.1 g of the IR-117, 0.2 g of CYASORB UV 24 Light Absorber and 10 g of plastic and injection molding. The sample was exposed in the FOM. After 100 hours of exposure, it was apparent that the Merlon M39F was not compatible with IR-117. The sample absorption had lifted extensively in the NIR.

In order to determine if the instability of the radical-cation type of infrared absorber in polycarbonate is due to the nature of the polymer

itself or due to additives, some unstabilized polycarbonate powder was obtained from General Electric Company. As a representative of a radical-cation, IR-117 was solvent cast from a methylene chloride solution of polycarbonate. Even with a UV absorber present, after 100 hours in an FOM unit, the IR-117 was extensively degraded. This would indicate that our absorbers are not stable in polycarbonate, and there appears to be little chance of stabilizing them in this substrate.

The near-infrared spectrum of the hydroxymethacrylate polymer, Hydron, coated on polycarbonate did not show any appreciable difference from that of the base polycarbonate.

CYASORB H-249 Infrared Absorber was molded in Lexan polycarbonate. The 60 mil thick sample had a luminous transmittance of 12.5% and O.D. of 6.1 at 0.6943 μm . This transmittance is too dark to be of use. After 500 hr of FOM exposure the transmittance was 11.5% and the O.D. at 0.6943 μm was over 5.5.

The Pd complex of dithiobenzoin was injection-molded in polycarbonate with excellent results. The color was a pleasing brown, with a luminous transmittance of 29%. The NIR absorption was strong from 0.800 to 1.0 μm . This could be useful for gallium arsenide protection, but not broad near-infrared laser radiation protection.

The product made by coupling squaric acid with β -naphthol was mixed with Lexan 141R polycarbonate and injection molded. This mix decomposed at the molding temperature of polycarbonate (about 500°F). Similar results were obtained when the tetrabutylammonium salt of nickel thionaphthol (λ max 1.06 μm) was molded in Lexan.

Using the following formulation several more absorbers were evaluated in polycarbonate:

500 g Lexan 141R Polycarbonate

0.2 g Infrared Absorber

1.5 g CYASORB UV 24 Light Absorber

The additives molded included:

- (1) Genacryl Blue salt of 1-mercapto-2-naphthol nickel complex
- (2) Bis(o-mercapto anilino)nickel
- (3) Bis(o-phenylenediamino)nickel
- (4) "Neutral" β -naphthol mercapto nickel
- (5) $(\text{Bu})_4\text{N}^+$ Salt of bis(toluenedithiol)nickel complex
- (6) Palladium dithioanisoin
- (7) Nickel dithioanisoin
- (8) "Neutral" bis(toluenedithiol)nickel

Numbers 1 through 5 and 8 decomposed on molding in polycarbonate at 510°F. Numbers 6 and 7 came out well. The Pd dithioanisoin (R8203-46-1) had a strong peak centered at 0.960 μm with a Y value of 64-65%. The Ni dithioanisoin (R8203-46-2) bottomed out from 0.900 to 0.960 μm , with the peak centered at 0.930 μm and a Y value of 55%. However, neither of these would be useful for the 1.06 μm line of an Nd laser. They do represent some of the only materials to withstand molding in polycarbonate and retain NIR absorption.

We prepared a formulation of absorbers for the UV and visible lasers for molding in polycarbonate.

500 g Lexan 141R
 0.05 g Orange Z-7078
 0.05 g "Genacryl Blue (SbF_6^- salt)
 0.45 g CYASORB H-249 Infrared Absorber
 1.5 g CYASORB UV 24 Light Absorber

This molded well and gave the following results:

| | O.D. | | | | | | |
|---------------------|-------------|-------------|-------------|--------------|-------------|-------------|--------------|
| λ (μ) | 0.322 μ | 0.337 μ | 0.488 μ | 0.5145 μ | 0.530 μ | 0.633 μ | 0.6943 μ |
| 17-18 | 5.5+ | 5.5+ | 0.8 | 0.8 | 0.7 | 2.1 | 3.8 |

To get an O.D. of at least 3.0, more Genacryl Blue SbF_6^- salt is needed, as well as more Orange Z-7078. This was labeled R8203-43A.

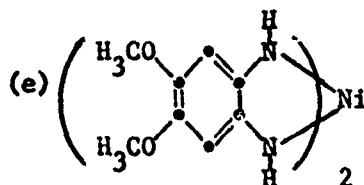
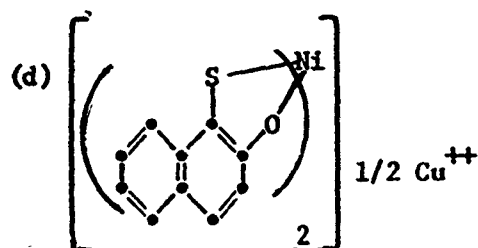
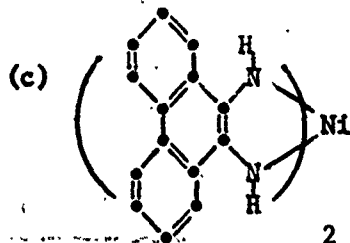
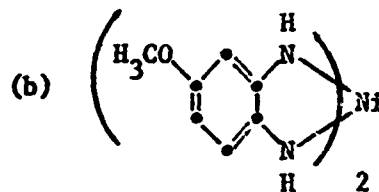
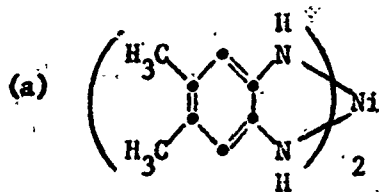
3. Polymethyl Methacrylate

Current pilot's visors are made predominantly from polymethyl methacrylate (PMMA) with a small quantity of visors of polycarbonate available. The absorbers, which we intended to use were not compatible with polycarbonate, so our emphasis was on PMMA in terms of visors or sheet.

Castings of methyl methacrylate with propylene glycol and glycerine were tried at a 2% level. The glycerine was not compatible and exuded from the cast sheet. While the propylene glycol was compatible, it did not give any appreciable absorption in the 1.9 to 2.3 μ m region.

Several inorganic copper salts were tested in methyl methacrylate monomer, but none were soluble. Those tried included: $\text{CuCl}_2 \cdot \text{H}_2\text{O}$; CuCl_2 (anhydrous); and $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$.

Monomer castings in methyl methacrylate were attempted on the following compounds, but none were soluble in the casting syrup.



The materials previously screened in solvents for absorption in the 2.0 to 2.5 μ m range, Table XI, were evaluated for candidates to incorporate into cellulose propionate or methyl methacrylate. However, none were found which had adequate absorption.

To evaluate NIR absorbers and set up cure cycles, the mixes shown in Table XVI were prepared.

Sheets A-D were undercured, and the casting cells were difficult to open. Thus, in cells E-H, a higher level of AIBN catalyst was used. Samples A-D also indicated that IR-126 was better than IR-117 in cast sheets and that less IR absorber, in general, could be used.

Table XVI**PMMA Casting Mixes**

| <u>28203-32-</u> | <u>Formulation in Grams</u> | | | | | | | |
|---|------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | <u>A</u> | <u>B</u> | <u>C</u> | <u>D</u> | <u>E</u> | <u>F</u> | <u>G</u> | <u>H</u> |
| PMMA Syrup | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| CYASORB IR-282 Infrared Absorber | 0.06 | 0.06 | - | - | 0.03 | 0.03 | - | - |
| CYASORB IR-117 Infrared Absorber | 0.2 | - | 0.2 | - | - | 0.15 | - | 0.15 |
| CYASORB IR-126 Infrared Absorber | - | 0.2 | - | 0.2 | 0.15 | - | 0.15 | - |
| CYASORB IR-99 Infrared Absorber | - | - | 0.06 | 0.06 | - | - | 0.03 | 0.03 |
| Irganox 1076 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| AIBN | 0.1 | 0.1 | 0.1 | 0.1 | 0.15 | 0.15 | 0.15 | 0.15 |
| CYASORB UV 24 Light Absorber | - | - | - | - | 0.2 | 0.2 | 0.2 | 0.2 |

The samples (E-H) were much better. The cure was better although the IR-117 samples were still somewhat troublesome. The data on the sheets are:

| <u>Sample</u> | <u>Y (%)</u> | <u>Absorbers Used</u> | <u>NIR</u> | <u>O.D. (1.06 μm)</u> |
|----------------------|---------------------|------------------------------|------------------------------------|---|
| (E) 28203-33A | 36 | IR-282; IR-126 | bottoms from 0.760-1.78 μ m | 4.5+ |
| (F) 28203-33B | 40 | IR-282; IR-117 | bottoms from 0.780-1.74 μ m | 4.5+ |
| (G) 28203-33C | 39 | IR-99; IR-126 | bottoms from 0.780-1.78 μ m | 4.5+ |
| (H) 28203-33D | 39 | IR-99; IR-117 | bottoms from 0.780-1.74 μ m | 4.5+ |

In these castings, IR-126 is far superior to IR-117 in retaining its activity through the cure cycle. Preliminary results are that IR-282 is better than IR-99. Light stability was run on these samples.

After 300 hours of FOM exposure, the monomer cast samples still look good. R8203-32A combines IR-126 with IR-282, and this looks the best.

R8203-32C combines IR-126 with IR-99 and this is almost as good. The data are:

| Sample | Y (Orig, %) | 300 Hr FOM Exposure | | O.D. | |
|-----------|-------------|---------------------|-------------------|--------------|---------------|
| | | Y (%) | NIR (% Remaining) | 1.06 μ m | 0.840 μ m |
| R8203-32A | 36 | 33 | 85.5 | 4.5+ | 4.5 |
| R8203-32C | 40 | 34 | 84.0 | 4.5+ | 4.5 |

The R8203-32B and -32C samples have IR-117 combined with IR-282 and IR-99, respectively. These samples are weaker in the NIR region.

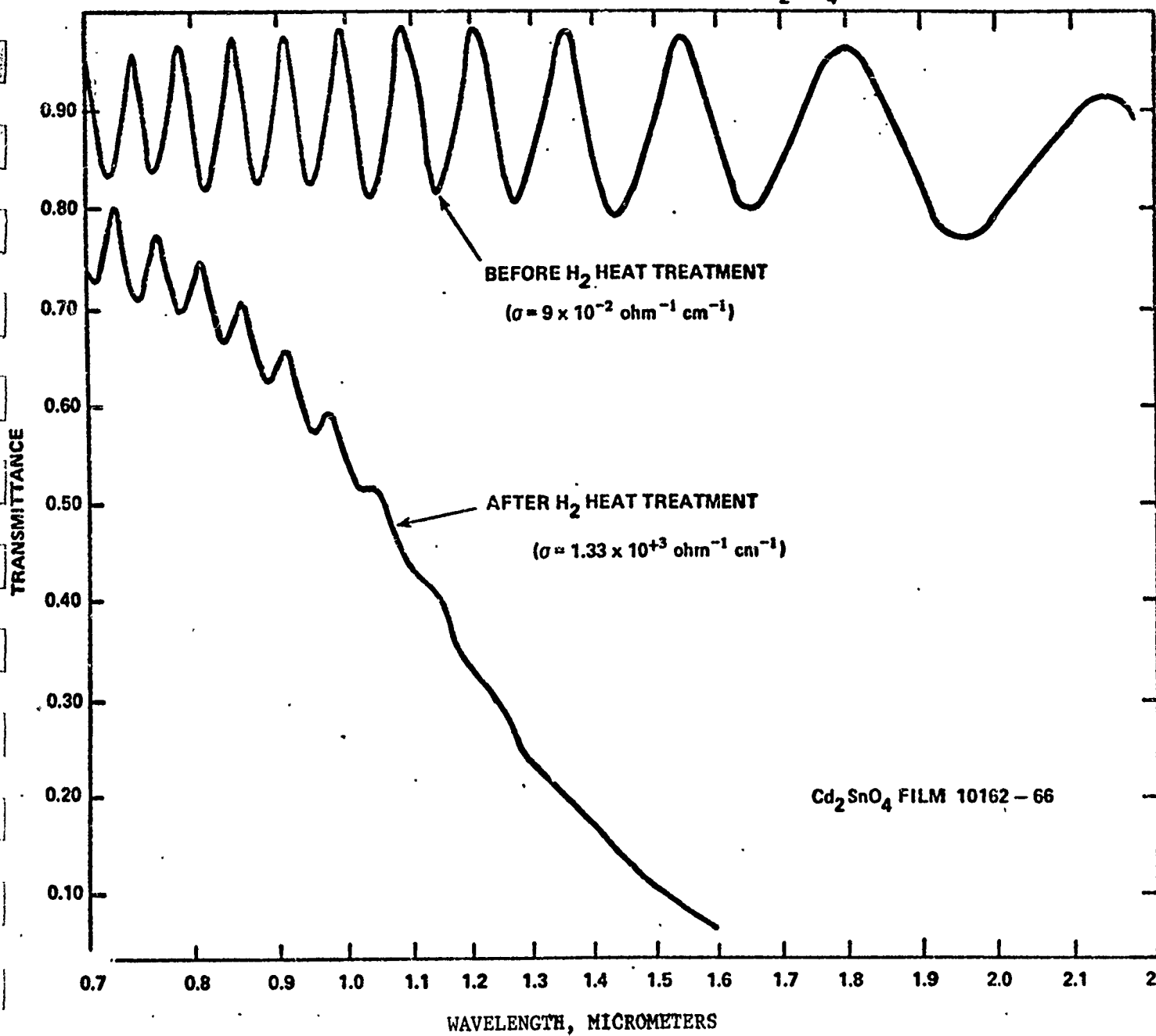
After 1,000 hours of FOM exposure, R8203-32A was still the best sample in terms of NIR retention. The sample had 79% of the NIR absorber remaining and O.D.'s of 4.5+ at 1.06 μ m and 4.3 at 0.840 μ m. Thus, formulation R8203-32A was used to provide the deliverable cast sheet.

4. Cadmium Stannate

It was believed that deficiencies in the IR absorption characteristics of the organic absorbers might be removed through use of Cd_2SnO_4 films absorbing all radiation with $\lambda > 1.7 \mu\text{m}$ (O.D. ≥ 3). Such absorption characteristics are exhibited by highly conductive Cd_2SnO_4 films supported on glass surfaces (e.g., film 10162-66 which had been heat-treated in H_2 at 280°C for 10 minutes, $\sigma = 1.3 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$). The near-infrared spectrum of this film is shown in Figure 4. Thus, we investigated the deposition of Cd_2SnO_4 with equivalent characteristics on cellulose propionate or Acrylite®.

Figure 4

NEAR IR TRANSMISSION SPECTRA OF Cd_2SnO_4 THIN FILMS



Our previous experience with the deposition of Cd_2SnO_4 on plastic surfaces showed that film reticulation is a serious problem. This problem is related to the mechanical stress induced in the Cd_2SnO_4 film by the difference in the coefficients of thermal expansion between substrate and film, as well as to the degree of film adhesion on the substrate. Studies were made on the relative importance of these two factors. These included surface treatments designed to improve adhesion, surface temperature measurements during sputtering, film thickness effects, and the differences in film-substrate coefficients of thermal expansion.

Samples of cellulose propionate used for laser-protective goggles were tried. These materials are plasticized and contain a liquid-like layer at their surface. Adhesion of Cd_2SnO_4 films to cellulose propionate was very poor, and no integral films could be deposited irrespective of surface treatment or film thickness.

The adhesion of Cd_2SnO_4 to Acrylite was much better; good thin films ($\sim 0.2\mu$) were easily deposited. However, the coefficient of thermal expansion (CTE) of Acrylite is about 100 times that of Cd_2SnO_4 ; this factor caused reticulation when the film thickness exceeded $\sim 0.2\mu$.

The first approach to solving this problem was Acrylite surface-treatment to enhance film adhesion. In a second approach, it was attempted to compensate for the difference in CTE by providing a plastic interlayer with a low glass transition temperature (T_g). In this way, the induced stresses could possibly be relieved by plastic flow during cooling of the sputtered film. Temperature measurements of the surface were made to determine the degree of stress involved.

The results of surface pretreatments are summarized in Table XVII. The chemical pretreatment was based on a procedure used to metallize plastics by electrodeposition, and involved the use of several baths for etching and activating the surface. The surface treatments described did not sufficiently increase adhesion to prevent reticulation of the thicker Cd_2SnO_4 films (1-3 μ).

Table XVII

Surface Pretreatment of Acrylite

| <u>Procedure</u> | <u>Result</u> |
|---|--|
| Chemical treatment according to U.S. 3,579,365 | Discoloration of the plastic when etching bath was hot ($T > 70^\circ\text{C}$); reticulation of thick film not prevented. |
| Exposure of surface to UV for 24-72 hours (in Weather-Ometer). | Reticulation of thick films not prevented. |
| Exposure of surface to O_2 -plasma (surface etching). | Reticulation of thick films not prevented. |
| Use of molded Acrylite containing <u>no</u> mold-release compounds. | Reticulation of thick films not prevented. |
| Deposition of thin SiO interlayer. | SiO did not adhere to Acrylite. |

The temperature at the Acrylite surface during sputtering was measured by embedding a small thermocouple in the surface of a 1/8" sample; the effects of RF power and chamber pressure are presented in Table XVIII.

Table XVIII

Effect of Power and Pressure on Surface Temperature

| <u>RF Power, watts</u> | <u>Chamber Pressure, μ (of Hg)</u> | <u>Surface Temperature, $^{\circ}\text{C}$</u> |
|------------------------|---|---|
| 60 | 13 | 98 |
| 60 | 6 | 86 |
| 100 | 6 | 100 |
| 150 | 6 | 118 |
| 200 | 6 | 136 |

These temperatures are relatively high, even at the lowest practical power level of 60 watts. The samples rested on a water-cooled platform, and the surface temperature reached its equilibrium value within 30 minutes.

Stresses in the film created during cooling of the sample after sputtering are severe if the CTE's of Cd_2SnO_4 and substrate are significantly different. The CTE's of all materials upon which Cd_2SnO_4 has been sputtered without reticulation problems is $\sim 21 \times 10^{-6}$; this, therefore, represents a practical upper limit for the CTE of untreated substrates. These results are summarized in Table XIX.

Table XIX

Film Formation on Various Substrates

| <u>Substrates which Exhibit No Problem with Film Reticulation</u> | <u>CTE, $\times 10^6$</u> |
|---|--------------------------------------|
| Glass | 2-10 |
| Fused Quartz | 1 |
| Metals (Cu, Fe, Ni, Al) | 10-20 |
| Silicon | 7 |
| BaF ₂ | 21 |
| <hr/> | |
| <u>Substrates which Cause Film Reticulation</u> | |
| Acrylite | 70 |
| NaCl | 40 |

The glass transition temperature of Acrylite is 105°C, and, therefore, the material is brittle over most of the temperature range encountered before and after sputtering. If a layer of material with T_g near room temperature could be deposited in the Acrylite before sputtering, the thermally induced stress could possibly be relieved by plastic flow in this layer. A polymer consisting of a polyvinylidene fluoride and polyethyl (or methyl) methacrylate mixture was available (T_g = 25°C, compatibility with Acrylite, visible transparency). Samples of this material were used as substrates, and Cd₂SnO₄ films of unusual strength and adhesion were easily deposited by sputtering. In fact, the substrates could be bent at 90° angles without fracturing or peeling the Cd₂SnO₄ film. Further development of this approach could concentrate on depositing a layer

of the PVdF-PEMA polymer on Acrylite by either hot-pressing a film or by forming a solution of the polymer and subsequently coating the surface.

Cd_2SnO_4 films heat-treated in H_2 at 280°C have maximum IR absorption. Since Acrylite cannot be heated above $\sim 100^\circ\text{C}$, and no reduction occurs below $\sim 250^\circ\text{C}$, the required IR absorption must be achieved by sputtering thick films in pure argon. From the electrical conductivity of films sputtered in argon ($\sim 1/3$ that of films heated in H_2 at 280°C), it is estimated that a film thickness of $\sim 10\mu$ is required to achieve the desired IR absorption. A sample (10162-126) consisting of a double layer of a fractured Cd_2SnO_4 film with a total thickness of about 5μ (formed by placing back-to-back two $1/8''$ Acrylite samples with 2.5μ thick Cd_2SnO_4 films) was evaluated. We measured a transmittance of $\sim 13\%$ at 1.7μ in this sample. Since the IR absorption is due to free carriers, the absorption coefficient increases with the second or third power of wavelength. This is a desirable feature, as the specifications for the laser goggles call for general IR absorption out to 10μ . However, the plastic substrates themselves have good IR absorption beyond 3μ ; thus, the absorption of Cd_2SnO_4 in this spectral region is not necessary. In addition, the problems of application and maintenance of the Cd_2SnO_4 films on visors and goggles appear to require considerable work in order to determine possible utility. It was decided to abandon this approach, for the time being, and concentrate on absorbers which could be incorporated into the plastics.

5. Miscellaneous Polymers

Polyethylene Terephthalate

An attempt was made to use Eastman polyethylene terephthalate as the polymer for its impact properties. However, the NIR absorbers were not stable in this matrix, and decomposition was observed on injection-molding.

Polyamide Polymer

A new polymer with good impact properties and good clarity was evaluated with CYASORB IR-117 Infrared Absorber to see if it could be molded. The polymer, Trogamid T, a clear polyamide from Dynamit Nobel, was molded at 400 to 450°F. The IR-117 was completely degraded. Evidently, the near-infrared (NIR) absorber is not stable in this plastic, as IR-117 can be molded in polymethyl methacrylate at these temperatures.

Polyvinyl Chloride

The Pd complex of dithioanisoin was solvent-cast in a thin PVC film, as was the Pt complex of dithiobenzoin. After 200 hours of FOM exposure, the Pt complex became darker, while the NIR absorption remained about the same (absorption from 0.750 to 0.860 μm). The Pd complex lost strength in the NIR (originally "bottomed" from 0.910 to 1.03 μm). Exposure was stopped at this point. Both of the above films were stabilized with CYASORB UV 24 Light Absorber.

6. Physical System of Attenuating from 1.9-2.3 μm

Since no absorbers were found for this region, an attempt to get absorption in this region with water was made. A FOG-BAN® lens was obtained from Glendale Optical Company, which consists of two cellulose propionate

lenses heat-sealed together at the edges with a 3/16" air space. This fits into a standard "Softie" goggle frame. The air space was filled with water on a lens. This absorbed quite strongly from 1.88-2.5 μ m. A mixture of water and ethylene glycol (85:15) was found to be good also. This mixture would prevent freezing at lower temperatures.

If the FOG-BAN lenses could be molded with our current formulation, then the lens filled with the absorbing liquid, the window from 1.9-2.3 μ m might be eliminated. However, this particular solution to the problem would only work for that specific configuration and would not be applicable to monomer cast sheets.

The FOG-BAN lens configuration containing an absorbing liquid layer in the interspace was found to have too much refractive power to be useful as a laser-protective lens unit. The distortion through the lens was excessive.

C. Deliverable Items

On June 30, 1972, 25 each of Softie Laser Eye Goggles (item 0001AB) and 90 each of Goggle Filter Lenses (item 0001AC) were sent to Brooks Air Force Base. These are the designations for deliverables in Modification 1 of the subject contract dated 24 January 1972.

The 0001AB Goggles have the same lenses as item 0001AC. These lenses have a luminous transmittance of 40-42%. The goggle frames are opaque.

The 60 mil thick goggle lenses were molded at Glendale Optical Co., Inc. using the following formulation:

50 lb Eastman Cellulose Propionate
 2.18 g CYASORB® IR-99 Infrared Absorber
 50.20 g CYASORB® IR-126 Infrared Absorber
 68 g CYASORB® UV 24 Light Absorber

Optical densities for the 115 lenses are tabulated below.

| <u>Wavelength in μm</u> | <u>Optical Density</u> |
|---|------------------------|
| 0.30-0.40 | 5 |
| 0.6943 | 0.9 |
| 0.84 | 3 |
| 1.06 | 4 |
| 0.78-1.76 | 3 min |
| 1.8-2.2 | <1 |
| 2.2-2.4 | 2-3 |
| 2.4-2.75 | <1 |
| 2.755-14.0 | 3 min |

The cast acrylic sheet, item 0001AA in Modification 1 of the contract, was prepared using the following formulation:

2,700 g Acrylic Casting Syrup
 0.675 g CYASORB® IR-282 Infrared Absorber
 3.75 g CYASORB® IR-126 Infrared Absorber
 0.54 g Irganox 1076
 5.4 g CYASORB® UV 24 Light Absorber
 4.05 g AIBN

A total of 14 sheets were sent to Brooks Air Force Base. Each sheet was approximately 13" x 12.5" x 0.100", or 1.128 square feet. Thus, a total of 15.8 square feet was sent.

There were 7 perfect sheets sent, and 7 sheets containing a few small air bubbles per sheet.

The cast filter sheets were our Reference Numbers R8203-134B, -134C, -134D; R8203-135A, -135B, -135C, -135D, -135E; and R8203-137A, -137C, -137D, -137E, -137F.

The filter material has a luminous transmittance of 35%.

Following is a tabulation of optical densities of the cast acrylic filters.

| <u>Wavelength in μm</u> | <u>Optical Density</u> |
|---|------------------------|
| 0.30-0.40 | 5+ |
| 0.6943 | 1 |
| 0.84 | 4 |
| 1.06 | 4 |
| 0.78-1.76 | 3 min |
| 1.8-2.2 | <1 |
| 2.2-2.4 | 2-3 |
| 2.4-2.75 | <1 |
| 2.755-14.0 | 3 min |

III. CONCLUSIONS

The synthetic search for new absorbers concentrated on the Type II and Type III structures. Since many compounds of these structures were examined, some conclusions can be drawn with respect to their chemical constitution and spectral properties.

A. Spectral Correlations of Some Near-Infrared Absorbers

1. Substituent Effects

In the Type A compounds (the aromatic dithiolates), according to G. N. Schrauzer's theory (12-14), we have chelate systems in which the ligands and the metal p-orbitals can be considered as being part of an electronic system similar to organic compounds with delocalized ground states. In compounds 1, 4 and 5 (Table IV) we see the spectral effect of putting substituents on the benzene ring of these chelates is essentially the same as that found for a regular polysubstituted benzene ring. In comparing compounds 1 and 4, the additional placement of two methyl groups on the respective rings in compound 4 shifts the λ max in compound 1 from 0.89 μ m to 0.90 μ m in compound 4. The effect of replacing the methyl groups in compound 4 with methoxyl groups on the spectrum of compound 5 is in keeping with results found in the literature. Since methoxyl groups have been shown to be greater electron releasing groups than methyl, the shift in λ max of compound 4 from 0.90 μ m to 0.95 μ m in compound 5 is in keeping with known substituent results in aromatic systems. The size of the shift (0.05 μ m) is considerable, but unfortunately with our present level of knowledge of these systems, it is not possible to account for the magnitude of the spectral result.

The Type E compounds (the diamine analogs of the Type A compounds), Table VII, with a fused aromatic ring on the basic diamino ring system show the greatest substituent effect in going from methyl to O-methyl on the benzene ring. It should be noted in examining the spectral data of compounds 1, 6 and 7, only a small bathochromic shift in the spectrum of compound 1 (λ max 0.78 μ m) is obtained by the substitution of one methyl group (compound 6, λ max 0.785 μ m) or two methyl groups (compound 7, λ max 0.79 μ m) on each benzene ring. In the case of compound 5, with O-methyl replacing methyl, a large dramatic shift of 0.215 μ m is observed (λ max 1.0 μ m for compound 5).

A possible mechanism for this anomalously large bathochromic shift could involve a quinoidal through conjugation resonance structure with a partial positive charge residing on the oxygen and a partial negative charge on the nitrogen or the metal atom. It should be pointed out that the weighting factor for any resonance structure is dependent on such factors, for example, as the separation of charge, which in this case would be sufficient to include this structure as a meaningful part of the total electronic structure of these compounds. The placement of an additional O-methyl group should be additive, but at the same time have only a relatively small effect if the aforementioned concept has some validity. The λ max for compound 8 (i.e., with two O-methyl groups on each benzene ring) is at 1.02 μ m which is only 0.02 μ m to the red of compound 5. The relatively small spectral shift, then, would be in keeping with our interpretation.

The Type F compounds with mixed chelating ligands of sulfur and nitrogen on an aromatic ring show anomalous results when bridged with glyoxal and biacetyl (Table VIII). By bridging compound 1 with glyoxal to give the

cyclic Schiff base derivative compound 4, a bathochromic shift of some 0.165 μ is obtained (from 0.565 μ for compound 1 to 0.73 μ for compound 4). If an increase through conjugation effect is invoked to account for this dramatic spectral shift, it is then somewhat puzzling to observe the decrease in absorptivity and hypsochromic shift of compound 6 (i.e., compared to compound 4) with two methyl groups. In general, as has been shown above, the inductive effect of the methyl group can account for some increase in the wavelength of the λ max for these systems. It would seem in the case of these bridged derivatives, the methyl groups while releasing electrons into the system may be also stabilizing the ground state with respect to the excited state, and thereby causing the hypsochromic shift.

In the Type III dithiolates, instead of having a substituted fused-aromatic ring system, these systems have various substituents attached to the basic dithio glycol 5-membered ring ligand (Table II). The λ max of compounds 5, 8, 10, 12 combine electron releasing effects and in some cases increased conjugation between the aromatic substituents and delocalized ground states of the basic dithiolate-metal system. In compounds 6 and 12, the electron releasing and conjugative effect of the phenyl substituents of the latter over the electron releasing and hyperconjugative effect of the methyl groups in the former is apparent with spectral shift of λ max in compound 6 of 0.773 μ to 0.565 μ in compound 12. The increased bathochromic shifts for compounds 8 and 10 over that of compound 12 demonstrates the electron releasing power of the aromatic heterocyclic oxygen and sulfur atoms. The slight shift in going from oxygen to sulfur (that is, from compound 8 to compound 10) is a reflection of the increased electron releasing power of sulfur over oxygen.

The substituted derivatives of compound 11 (i.e., compounds 20, 22 and 25) show the effect of *O*-alkyl substituent on the absorption spectrum of these dithiolates chelates. In compound 25, the *O*-methyl substituent which is located on only one part of the phenyl substituted dithiolate system shifts the λ max of compound 12 from 0.865 μ m to 0.895 μ m for compound 25. The addition of *O*-methyl groups on the other side of compound 25 (i.e., compound 20) shift the λ max of compound 25 from 0.895 μ m to 0.920 μ m for compound 20.

Replacing the methyl group with *n*-butyl (i.e., compound 22), shifts the λ max of compound 20 from 0.920 μ m to 0.930 μ m for compound 22. This slight increase of *O*-*n*-butyl over *O*-methyl reflects the greater electron releasing power of the substituent with longer alkyl chain.

2. The Effect of Different Metal Atoms

In the various types of chelates discussed in the preceding Subsection 1, we dealt with systems that all had nickel as the chelated metal atom. In this Section, the results that were found with other metals will be shown with the implied criterion of stabilization of the planar geometry with regard to the molecular orbital of the ligand system, and the interaction of the metal *p*-orbitals with the former. On the basis of this general interpretation and without going into a complicated description of the relevant π -MO's of the ligand and atomic orbitals of the metal, the size of the bathochromic shift and, to some degree, the magnitude of the molecular extinction coefficient will be a function of the degree to which a given metal interacts with the chelating ligands. That is, the greater the shift and increase in absorptivity of the spectrum, the greater the interaction between electronic orbitals of the metal atom and the molecular orbitals of the ligand.

Some examples are to be found for several classes of transition metals in the various types of compounds illustrated in Tables IV-IX. The metal-ligand systems which seem to have the greatest absorptivity at longer wavelengths are based on Group VIII transition metals represented by nickel, palladium, and platinum. In general, the platinum compounds absorb at somewhat shorter wavelengths than nickel and palladium but with greater absorptivity. Some examples of these general statements are to be found in Table XX.

A bathochromic shift appears to take place in changing the metal from cobalt, to osmium to platinum to nickel and to palladium (compounds 11, 13, 15, 12 and 14, also compounds 16, 17, 20 and 21 of Table IX).

Table XX

| Reference Table | Compounds and NIR Spectra | | | | | |
|--------------------|---------------------------|--------------------------|--------------|--------------------------|--------------|--------------------------|
| | Pt | | Ni | | Pd | |
| | Comp. No. | λ max (μ m) | Comp. No. | λ max (μ m) | Comp. No. | λ max (μ m) |
| IV | 6 | 0.89 | 5 | 0.95 | 8 | 0.98 |
| V | 6 | - | 3 | (1.06 (1.62* | 5 | 1.64* |
| VII | 9 | 0.89 | 8 | 1.02 | 11 | 1.08 |
| VII | 4 | 0.711 | 1 | 0.78 | 3 | 0.78 |
| VIII | - | - | 1 | 0.865 | 3 | 0.865 |
| IX | 15 | 0.80 | 12 | 0.865 | 14 | 0.885 |
| IX | 17 | 0.863 | 20 | 0.92 | 21 | 0.948 |
| IX | ? | 0.74 | 6 | 0.773 | - | - |

*Not λ max, secondary peaks.

3. The Effect of Additional Fused Aromatic Rings

The effect of fusing additional aromatic rings either linear^{1/} or angularly on an aromatic system (e.g., benzene \rightarrow naphthalene) is an increase in the wavelength of $\pi \rightarrow \pi^*$ transitions. If these systems are indeed "aromatic" systems as described by Schrauzer (12-14), then, the very same spectral effect should be observed in going from the fused-ring benzene compound to higher order derivatives such as the naphthalene system.

Several examples are compounds 1, 3, 4 of the Type B materials (Table V). In going from the benzene ring in compound 1 to naphthalene ring in compound 3, we see a small red shift and a decrease in absorptivity of the main band from 1.02 μm ($a = 25.5$) in compound 1 to 1.06 μm ($a = 17.1$) in compound 3. However, in the case of compound 3 we have picked up two additional bands in the near-infrared located at 1.34 μm ($a = 9.8$) and 1.62 μm ($a = 4.1$). In addition, changing of the counter ion, tetra-*n*-butyl ammonium, in compound 3 for potassium in compound 4 yields the following near-infrared bands: 1.675 μm ($a = 7.5$), 1.565 μm ($a = 5.8$), 1.36 μm ($a = 15.9$), 1.185 μm ($a = 25.5$), and 1.1 μm ($a = 31.3$). In compound 4, there would appear to be combination of factors operating: (1) the increased conjugation effect of the additional ring, and (2) an increased polarization effect of the potassium ion over that of the tetra-*n*-butyl ammonium ion. Three additional examples are compounds 1, 12 and 14 of the Type E series. In these diamino analogs, as noted before, the spectral shifts are quite large. In going from the 1,2-diamino benzene-nickel system (compound 1) to the 1,2-diamino naphthalene, a near-infrared spectral shift of 0.25 μm is obtained (from 0.78 μm in compound 1 to 1.03 μm in compound 12). An additional substantial shift of 0.12 μm is noted in going

from compound 12 (λ max, 1.03 μ m) to 9,10-diamino phenanthrene system (compound 14, λ max, 1.15 μ m). Unfortunately, the ϵ values or molar extinction coefficients are not available for compounds 12 and 14. The very large spectral shift observed in these compounds is due to the probable importance of quinoidal structures in the electronic description of these materials. This same type of phenomenon was observed and commented on earlier in a discussion of the substituent effects on the same ortho-1,2-diamino aromatic-metal systems.

4. The Effect of N, S, O Coordination

The results are inconclusive on a study of the effect of nitrogen, sulfur, oxygen and various combinations of these three elements when coordinated to a metal. This is shown in Tables XXI and XXII. Some of the inconsistencies might be due to the impurity of the compound being used to make the measurement. Most of the compounds listed in the Section II A (Results) of this report were not thoroughly analyzed and structures definitely proven.

Table XXI indicates a change from dithiol coordination to oxygen-nitrogen coordination gives a hypsochromic shift of about 0.09 μ m (see compounds e and f).

The shift from a dioxide coordination to a thiol-oxide condensation (compounds a and b) cannot be compared, since compound a was black and insoluble.

A bathochromic shift of over 0.10 μ m seems to occur in changing from the mine-oxide structure to the thiol-oxide structure (compounds j and h). Compound j had visible absorption, but no NIR absorption, while compound h had a λ max in the NIR.

Table XXI

Change of Coordinating Group V or VI Atoms

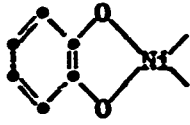
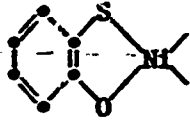
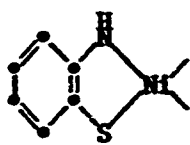
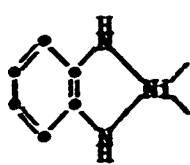

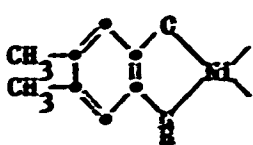
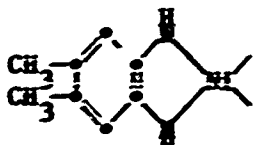
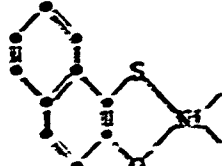
| <u>No.</u> | <u>Reference</u> | | <u>Structure</u> | <u>NIR λ max μs</u> |
|------------|------------------|-----------------|---|---|
| | <u>Table</u> | <u>Compound</u> | | |
| a | - | - |  | None determined |
| b | V | 1 |  | 1.02 |
| c | VIII | 1 |  | 0.865 |
| d | VII | 1 |  | 0.78 |
| e | IV | 4 |  | 0.90 |
| f | VI | 2 |  | 0.81 |
| g | VII | 7 |  | 0.79 |
| h | V | 3 |  | 1.06 |

Table XXI - Continued

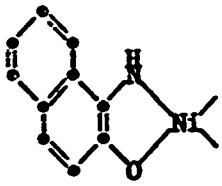
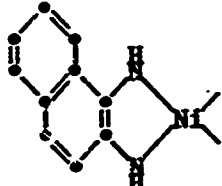
| <u>No.</u> | <u>Reference</u> | | <u>Structure</u> | <u>NIR λ max</u> <u>μ</u> |
|------------|------------------|-----------------|---|--|
| | <u>Table</u> | <u>Compound</u> | | |
| j | VI | 4 |  | None |
| k | VII | 12 |  | 1.03 |

Table XXII

Change from Dithiol Coordination to Diamine

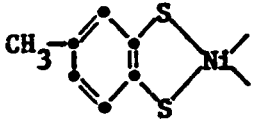
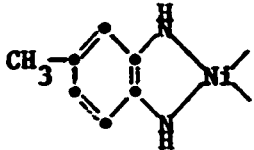
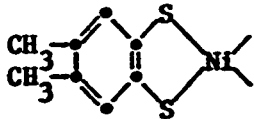
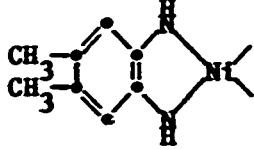
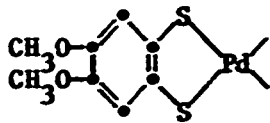
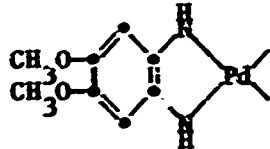
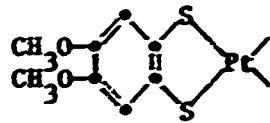
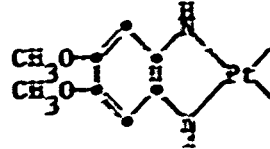
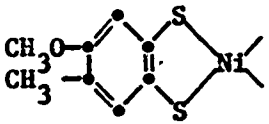
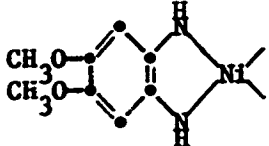
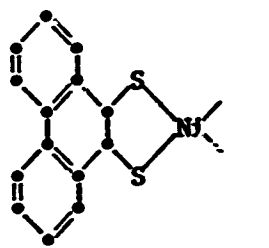
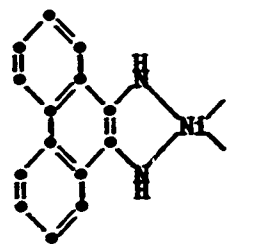
| No. | Reference | | Structure | λ max μm | Change μm |
|-----|-----------|----------|---|--------------------------------|-------------------------|
| | Table | Compound | | | |
| a | IV | 1 |  | 0.89 | - |
| b | VII | 6 |  | 0.785 | -0.105 |
| c | IV | 4 |  | 0.90 | - |
| d | VII | 7 |  | 0.79 | -0.11 |
| e | IV | 7 |  | 1.3 | |
| f | VII | 11 |  | 1.08 | -0.22 |
| g | IV | 6 |  | 0.89 | |
| h | VII | 9 |  | 0.89 | 0 |

Table XXII - Continued

| No. | Reference | | Structure | λ max μm | Change μm |
|-----|-----------|----------|---|--------------------------------|-------------------------|
| | Table | Compound | | | |
| j | IV | 5 |  | 0.95 | |
| k | VII | 8 |  | 1.02 | +0.07 |
| l | IV | 9 |  | 0.97 | |
| m | VII | 14 |  | 1.15 | +0.18 |

A bathochromic shift appears to take place when diamine coordination is changed to thiol-oxide coordination (compounds k-h and d-b).

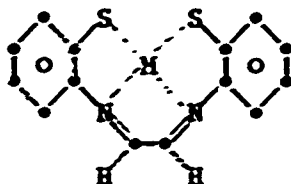
Comparing compounds a and d would seem to indicate little difference between dioxide and diamine coordination. Again the instability of the dioxide compound may have given us misleading data. This same situation is present with dioxide to thiol amine coordination (compounds a and c).

The effect of the change from diamine to amine-oxide is ambiguous, see compounds f-g and j-k. However, it would appear that changing from a diamine to an amine-thiol coordination gives a bathochromic shift of 80 nm.

Table XXII, gives examples of the change from dithiol coordination to diamine coordination. Compounds e and l are undoubtedly impure, since their λ_{\max} are not in keeping with the general pattern found in the other compounds.

B. Recommendations

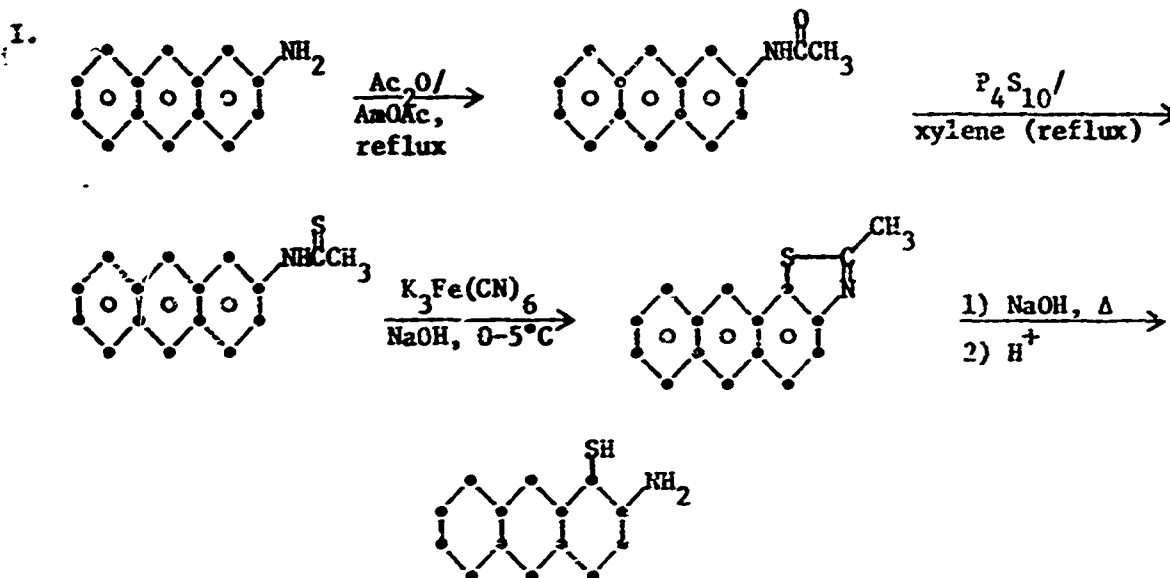
With the overall difficulty of preparing polycondensed, aromatic ring systems with the proper substituents ortho to each other and obtaining good thermal and photostability of the resulting chelates, the synthesis of such systems should be re-evaluated to seek a method which would yield the desired chelating ligand in the least number of steps and might afford the most stable system with the desired spectroscopic properties. The preparation, in this laboratory, of system (XV) which had a λ_{\max} at 1.03 and 0.81 μm , indicates that this type of structure might be of special interest because



XV

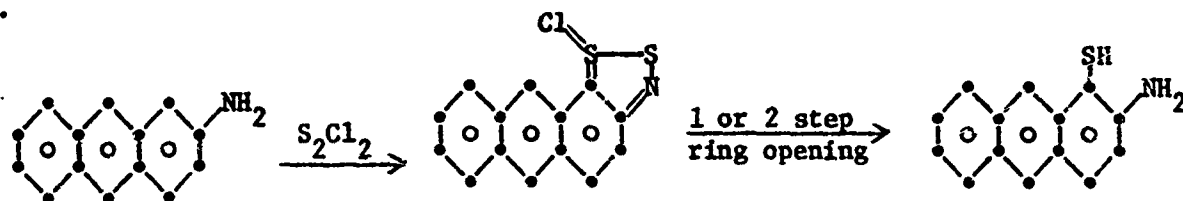
its λ_{max} values are at longer wavelengths than any of the other analogous systems incorporating a single benzene ring. Additional investigation of the possibility of developing other systems based on XV appears quite good, since an excellent way to form these materials is to start with an amino derivative (either in the 1 or 2 position) of a polycyclic aromatic, prepare a thio derivative, ring-close this compound in 1-2 steps, and then ring-open the latter to give the desired ortho-mercapto-amine derivative. This material is then reacted with glyoxal to yield the Schiff base (XV) (without M), which serves as the chelating ligand. The "tying-up" of the nitrogens through the formation of the Schiff base may add to the desired stabilization of these materials, since other compounds containing only the sulfur ligand, for possible "radical" participation in these complexes, have shown the desired thermal and photo-stability.

One of the systems of this type is 2-aminoanthracene. We have successfully carried out Step 1 in the reaction Scheme I outlined below.

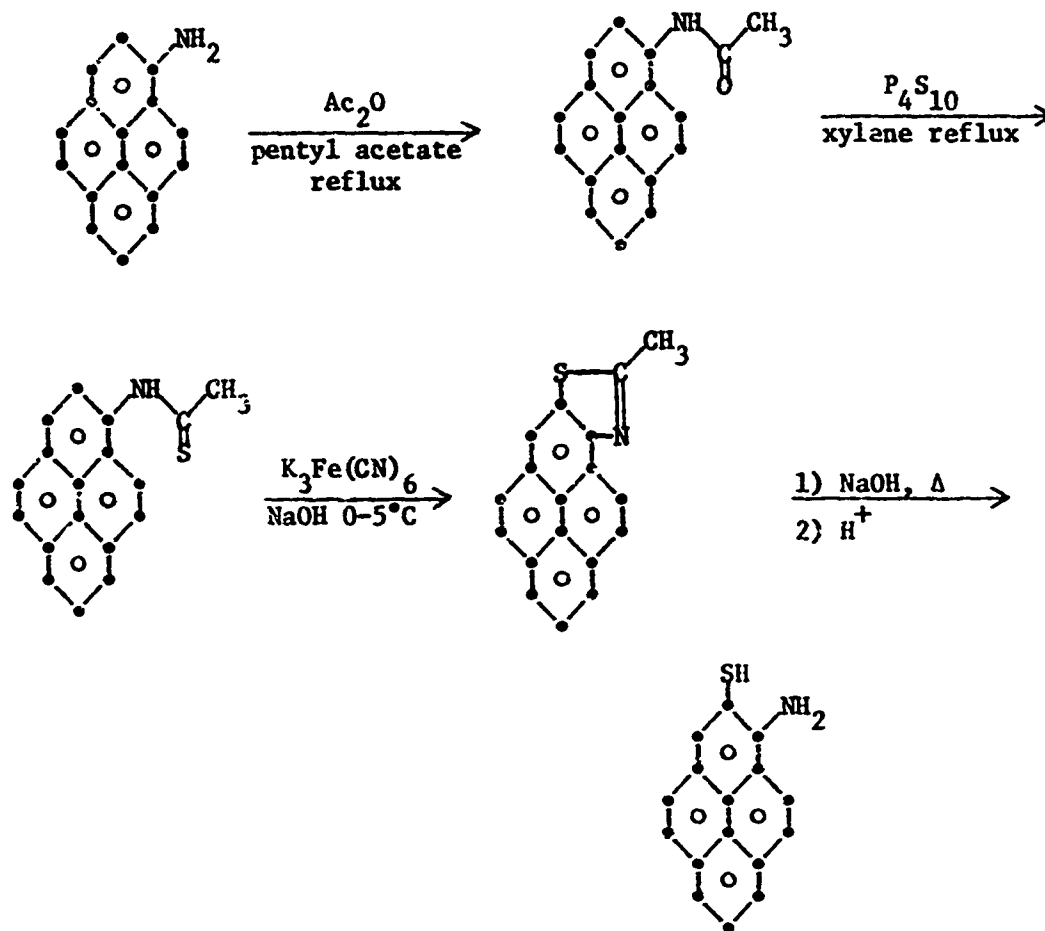


A much quicker, additional reaction plan is outlined below:

II.



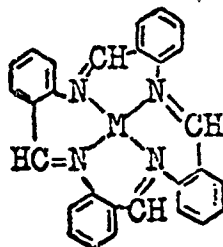
The reaction sequences should be pursued to obtain examples of these products. Pyrene derivatives also should be investigated, and could be made by reactions routes I or II as shown below.



We have prepared the N-acetyl derivative of 1-aminopyrene by the procedure shown. The compound was found to be pure enough (a reasonable melting point) so that no work-up will be required to use this material for the next step (the reaction with P_4S_{10}). This ligand can either be used as is to chelate a transition metal, or reacted with glyoxal to yield the di-Schiff base which would then be used as the chelating ligand.

Other compounds which might provide the necessary absorption from 1.5-2.5 μ m include the following:

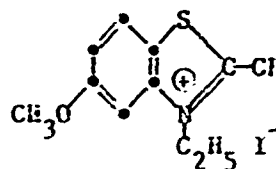
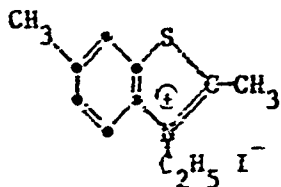
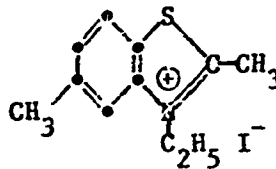
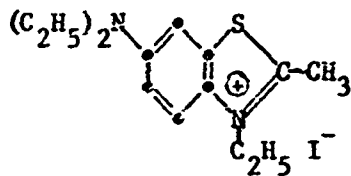
a. Metal chelates based on the tetradentate macrocyclic ligand from o-aminobenzaldehyde.



b. Condensation product diamines and 1-mercaptobenzaldehyde.

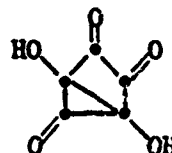
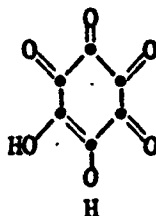
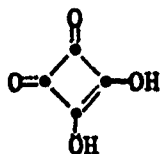
c. Metal complexes of dithiocarbamates.

d. Benzothiazoles such as:



e. Indoles and benzoxazoles.

f. Additional condensation products of squaric acid, rhodizonic acid, or croconic acid (Type V compounds).



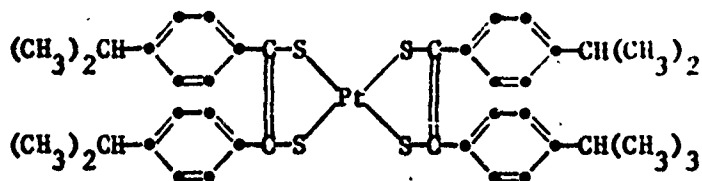
g. Additional Type II and Type III structures.

h. Polymers such as polyvinyl alcohol which might absorb very strongly.

For absorption in the 0.694 μm region, we would suggest synthesizing compounds of the following structures. The table below illustrates that a change of the coordinating metal alters the spectral features of the compounds.

| <u>Compound</u> | <u>Metal</u> | <u>λ max (μm)</u> |
|-----------------|--------------|--|
| | Co | 0.74, 0.62 |
| " | V | 0.80, 0.82 |
| " | Pt | 0.863 |
| " | Ni | 0.92, 0.927 |
| " | Pd | 0.948 |

If the methoxy group is replaced by an isopropyl group, the absorption appears to shift from the near-infrared toward the visible. For example,



has its absorption maximum at 0.828 μm .

We would suggest the synthesis of a variety of compounds having this general type structure which have selected metals as the coordination atom. These compounds would include aromatic nuclei possessing either electron-withdrawing or electron-contributing substituents.

Other compounds to investigate further for absorption at 0.694 μm would include the phthalocyanine compounds which have good absorption properties in the 0.60-0.70 μm spectral range but little or no absorption in the near-infrared region.

REFERENCES

1. A. E. Sherr, Plastic Compositions Capable of Absorption at Laser Wavelengths. Proceedings of the Laser Industry Association Convention, Washington, D.C., p 146 (October 24-26, 1968)
2. A. E. Sherr, R. J. Tucker and R. A. Greenwood, New Plastics Absorb at Laser Wavelengths, Laser Focus, 5 (No. 17): 46-48 (September 1969)
3. A. E. Sherr, R. J. Tucker and R. A. Greenwood, Plastic Filters for Laser Protection. International Laser Colloquium Sponsored by Electronics Industries Assn., Paris, France, pp 164-180 (Nov. 18-20, 1969)
4. J. F. Hosler and R. J. Tucker, Plastic Film Capable of Absorption at Specific Spectral Wavelengths (U) Phase I Research Report, AD-385,081-L, American Cyanamid Co., Bound Brook, N. J., May 1967
5. A. E. Sherr, J. F. Hosler and J. C. Oppelt, Plastic Film Capable of Absorption at Specific Spectral Wavelengths (U), Phase II Research Report, AD-844,720, American Cyanamid Co., Bound Brook, N. J., October 1968
6. A. E. Sherr and R. J. Tucker, Research and Development of an Ocular Laser Protective Filter (Plastic), Final Report on Contract F41609-69-C-0055, American Cyanamid Co., Bound Brook, N. J., September 1970
7. P. V. Susi and H. C. Donoian, Research on Absorbing Infrared Rays with Plastics and Alternating Infrared Rays with Coatings. Technical Report ARML-TDR-62-92. American Cyanamid Co., Bound Brook, N. J., August 1962
8. R. A. Coleman, A. E. Sherr and R. J. Tucker, Development of Absorptive and Reflective Lenses for Goggles and Helmet Visors. Technical Report ASD-TR-68-67. American Cyanamid Co., Bound Brook, N. J., April 1969
9. J. P. Fackler, Jr. and D. Conconvanis, Sulfur Chelates, III, Metal Complexes of the 1,1-Dithiolato Anions $S_2CS_2^-$, S_2CNCN^{2-} and $S_2CC(CN)_2^{2-}$. J. Am. Chem. Soc., 88 (17) 3913 (1966)
10. A. Davison, et al, The Preparation and Characterization of Four-Coordinate Complexes Related by Electron-Transfer Reactions. Inorg. Chem., 2 (6) 1227 (1963); Further Examples of Complexes Related by Electron-Transfer Reactions: Complexes Derived from Bis(trifluoromethyl)-1,2-dithiethane, Inorg. Chem., 3 (6), 814 (1964)
11. H. B. Gray, Electronic Structure of Square Planar Metal Complexes, pp 240-287 in Carlin, R. L. (ed) Transition Metal Chemistry, Vol. I, New York, Marcel Dekker, Inc. (1965)

REFERENCES - Continued

12. G. N. Schrauzer, et al, Coordination Compounds with Delocalized Ground States, Bisdithioketone Complexes of Iron and Cobalt, J. Am. Chem. Soc., 88 (20), 4604 (1966); Preparation, Reactions and Structure of Bisdithio- α -diketone Complexes of Nickel, Palladium and Platinum, J. Am. Chem. Soc., 87 (7), 1483 (1965)
13. G. N. Schrauzer, private communication.
14. O. Siimann and J. Fresco, Infrared Spectra of Divalent Metal Dithioacetylacetonates, Inorg. Chem., 8 (9), 1846 (1969)
15. G. C. Allen and N. S. Hush, Reflectance Spectrum and Electronic States of the CuCl_5^{3-} Ion in a Number of Crystal Lattices, Inorg. Chem., 6 (1), 4 (1967)
16. F. Kaufman and D. O. Cowan, The Organic Solid State Electron Transfer in a Mixed Valence Salt of Biferrocene, J. Am. Chem. Soc., 92, (1) 219, The Organic Solid State. III. Spectroscopic and Electrical Properties of Biferrocene [Fe (II) Fe (III)] Picrate, 92 (21) 6198 (1970)
17. R. Williams, et al, The Toluenedithiolate and Maleonitriledithiolate Square-Matrix Systems, J. Am. Chem. Soc., 88 (1), 43 (1966)
18. A. L. Balch, Electron-Transfer Series of the $[\text{M}-\text{O}_2\text{S}_2]$ Type. Complexes Derived from o-Mercaptophenol, 1-Mercapto-2-naphthol, and 1-Hydroxy-2-pyridinethione, J. Am. Chem. Soc., 91 (8), 1949 (1969)
19. H. A. Stevenson and S. Smiles, β -Naphtha-1-thioquinone and Dehydro-2-naphthol-1-disulfide, J. Chem. Soc., 1930, 1740
20. A. L. Balch, F. Röhrschud and R. H. Holm, New Systems of Complexes Related by Electron-Transfer Reactions, J. Am. Chem. Soc. 87 (10), 2301 (1965)
21. A. L. Balch and R. H. Holm, Complete Electron-Transfer Series of the $[\text{M}-\text{N}_4]$ Type, J. Am. Chem. Soc., 88 (22), 5201 (1966)
22. H. Jadamus, Q. Fernando and H. Freiser, Metal Ion Induced Rearrangements of Bisbenzthiazolines to Schiff-Base Chelates, J. Am. Chem. Soc., 86, 3056 (1964)
23. R. H. Holm, et al, Electron-Transfer Complexes of the $[\text{M}-\text{N}_2\text{S}_2]$ Type. The Existence of Cation-Stabilized Free-Radical Complexes, J. Am. Chem. Soc., 89 (12), 2866 (1967)
24. S. M. Bloom, Plastic Optical Elements, U. S. Patent 3,588,216 (June 28, 1971)

REFERENCES - Continued.

25. G. N. Schrauzer, et al, Metal Complexes Containing Sulfur,
German Patent 1,211,626 (March 3, 1966)
26. American Standards Association Bulletin, "The Spectral-Transmissive
Properties of Plastics for Use in Eye Protection (1955)
27. R. Stair, Spectral-Transmissive Properties and Use of Eye-Protective
Glasses; Circular 471 U. S. Department of Commerce, National Bureau
of Standards (1948)